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WOODHOUSEITE AND SVANBERGITE IN HYDROTHERMAL ORE DEPOSITS: PRODUCTS OF APATITE DESTRUCTION DURING ADVANCED ARGILLIC ALTERATION

ROGER E. STOFFREGEN* AND CHARLES N. ALPERS**
Department of Geology and Geophysics, University of California, Berkeley, California 94720, U.S.A.

ABSTRACT

Woodhouseite and svanbergite, previously documented from roughly two dozen localities, have been found with advanced argillic alteration in three hydrothermal ore deposits. These aluminum phosphate–sulfate (APS) minerals are isostructural with alunite ($R\bar{3}m$), with the generalized formula $RAl_3(PO_4)_{1+x}(SO_4)_{1-x}(OH)_{6-x} \cdot (H_2O)_x$, where R is Ca or Sr, and x is less than 0.5. At Summitville, Colorado, an epithermal gold-copper deposit, svanbergite occurs with hypogene kaolinite and alunite in the upper portions of the deposit, and woodhouseite is observed at deeper levels, where pyrophyllite is locally abundant. In the porphyry-copper deposit at La Granja (Peru), woodhouseite occurs with pyrophyllite and appears to have replaced apatite. The porphyry-copper deposit at La Escondida (Chile) contains woodhouseite–svanbergite solid solutions, some hypogene, others supergene, as judged from textural criteria. Alunite specimens from Summitville, La Escondida, and several other localities investigated in this study contain some APS component, with up to 2.41 wt.% P_2O_5 and 1.12 wt.% SrO, reflecting the coupled substitution $K^+ + SO_4^{2-} = (Ca,Sr)^{2+} + PO_4^{3-}$ in the alunite structure. The APS phases are considered to form by replacement of apatite in the acidic, sulfate-rich environment that characterizes advanced argillic alteration. Their occurrence probably has been overlooked in many areas showing such alteration of apatite-bearing host rocks.

Keywords: svanbergite, woodhouseite, alteration (advanced argillic), alunite, apatite, ore deposits.

SOMMAIRE

Woodhouséite et svanbergite, identifiées à ce jour dans environ deux douzaines d'endroits, ont été trouvées dans trois gîtes minéraux hydrothermaux, caractérisés par une altération argilacée avancée. Ces deux espèces, de composition sulfate–phosphate d'aluminium (APS), sont isotypes de l'alunite ($R\bar{3}m$). Elles répondent à la formule généralisée $RAl_3(PO_4)_{1+x}(SO_4)_{1-x}(OH)_{6-x} \cdot (H_2O)_x$, avec R = Ca ou Sr et $x < 0.5$. A Summitville (Colorado), la svanbergite se trouve dans un gîte cuivre–or épithermal, où elle se présente, avec kaolinite et alunite hypogènes, dans la partie supérieure du gisement, tandis que la woodhouséite se rencontre à des niveaux inférieurs, où la pyrophyllite est localement abondante. Dans le gîte de La Granja (Pérou), la woodhouséite se présente avec de la pyrophyllite dans le porphyre cuprifère, où elle aurait remplacé l'apatite. Le porphyre cuprifère de La Escondida (Chili) contient des solutions solides woodhouséite–svanbergite, les unes hypogènes, les autres supergènes, à en juger d'après les critères texturaux. Des spécimens d'alunite de Summitville, La Escondida, et plusieurs autres gîtes étudiés, contiennent un constituant APS, dont la teneur en P_2O_5 atteint 2.41% en poids, avec 1.12% en poids de SrO. Ces chiffres reflètent la substitution accouplée $K^+ + SO_4^{2-} = Sr^{2+} + PO_4^{3-}$ dans la structure cristalline de l'alunite. Les phases APS se seraient formées par remplacement de l'apatite dans le milieu acide et riche en sulfate, caractéristique d'une altération argilacée avancée. Ces phrases seraient passées inaperçues dans plusieurs examples d'une telle altération de roches hôtes porteuses d'apatite.

(Traduit par la Rédaction)

Mots-clés: svanbergite, woodhouséite, altération argilacée avancée, alunite, apatite, gîtes minéraux.

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*Present address: Department of Geological Sciences, Southern Methodist University, Dallas, Texas 75275, U.S.A.

**Present address: Department of Geological Sciences, 1006 C.C. Little Building, University of Michigan, Ann Arbor, Michigan 48109-1063, U.S.A.

INTRODUCTION

The behavior of phosphate minerals during hydrothermal alteration has received little attention in the literature. This is in contrast to numerous studies on phosphate minerals in the weathering cycle (*e.g.*, Nriagu 1976, Vieillard *et al.* 1979, de Lima & Reymão 1983), and on the complex mineralogy of phosphate-rich pegmatites (*e.g.*, Moore 1973). Apatite is the most common phosphate mineral in igneous rocks, where it generally occurs as an accessory phase. Apatite also occurs as a trace phase in the zone of potassic alteration developed in porphyry-copper deposits (*e.g.*, Gustafson & Hunt 1975, Reynolds 1985), and it can occur with sericite in vein mineralization (*e.g.*, Kelly & Rye 1979). However, apatite has not been reported in the "advanced argillic" alteration zone, generally characterized by alunite and aluminosilicate minerals (Meyer & Hemley 1967). This suggests that apatite may be dissolved or replaced by another phosphate mineral in the acidic, sulfur-rich environment required for this type of alteration.

We discuss here the occurrence of such a mineral, with the generalized chemical formula $R\mathrm{Al}_3(\mathrm{PO}_4)_{1+x}(\mathrm{SO}_4)_{1-x}(\mathrm{OH})_{6-x}{\bullet}(\mathrm{H}_2\mathrm{O})_x$, in the advanced argillic zones of three hydrothermal ore deposits. Specifically, we consider woodhouseite and svanbergite, the Ca and Sr end-members for which $x = 0$, and solid solutions between these two minerals and members of the crandallite–goyazite series, for which $x = 1$. Formulae for these and other aluminum phosphate–sulfates are listed in Table 1.

Woodhouseite, svanbergite, and the other aluminum phosphate-sulfate (APS) minerals listed in Table 1 belong to an isostructural group of minerals that have the generalized formula $RA_3(X\mathrm{O}_4)_2(\mathrm{OH})_6$, where R is a monovalent, divalent, or trivalent cation, A is a trivalent cation, generally Al^{3+} or Fe^{3+}, and X is either sulfur, phosphorus, or arsenic (Botinelly 1976). Perhaps the most common of these minerals is alunite $\mathrm{KAl}_3(\mathrm{SO}_4)_2(\mathrm{OH})_6$, which occurs mainly as a vein mineral or alteration product of feldspars and micas in sulfur-rich, highly oxidized environments (Hemley *et al.* 1969).

TABLE 1. ALUMINUM PHOSPHATE (SULFATE) END-MEMBER COMPOSITIONS

Svanbergite	$\mathrm{Sr\ Al_3\ (PO_4)\ (SO_4)\ (OH)_6}$
Woodhouseite	$\mathrm{Ca\ Al_3\ (PO_4)\ (SO_4)\ (OH)_6}$
Hinsdalite	$\mathrm{Pb\ Al_3\ (PO_4)\ (SO_4)\ (OH)_6}$
Goyazite	$\mathrm{Sr\ Al_3\ (PO_4)_2\ (OH)_5{\cdot}H_2O}$
Crandallite	$\mathrm{Ca\ Al_3\ (PO_4)_2\ (OH)_5{\cdot}H_2O}$
Gorceixite	$\mathrm{Ba\ Al_3\ (PO_4)_2\ (OH)_5{\cdot}H_2O}$
Florencite	$\mathrm{Ce\ Al_3\ (PO_4)_2\ (OH)_6}$

Substitution of one mole of PO_4^{3-} for SO_4^{2-} in alunite creates an excess negative charge, which can be compensated by substitution of an equimolar amount of a divalent cation on the R position. Our findings suggest a limited degree of this coupled substitution

$$\mathrm{SO}_4^{2-} + R^{+} = \mathrm{PO}_4^{3-} + R^{2+} \qquad (1)$$

in samples of natural alunite formed at temperatures below 300°C, although at higher temperatures a more extensive solid-solution may exist.

In the APS minerals *woodhouseite* and *svanbergite,* half of the SO_4^{2-} groups in the alunite structure are replaced by PO_4^{3-}, and all of the monovalent cations are replaced by the divalent cations Ca^{2+} and Sr^{2+}, respectively. This coupled substitution has little effect on crystal structure, as these minerals have the same symmetry as alunite (space group $R\bar{3}m$) and only slightly modified a and c parameters, as noted by Pabst (1947), Kato (1971, 1977) and Kato & Miura (1977).

In addition to variation in the amount of Sr and Ca in the R site, we have observed substantial deviation from a 1:1 ratio of sulfate to phosphate in the X site. An increase in phosphate above one mole per formula unit at the expense of sulfate requires further compensation of charges, which can be achieved either by the addition of a trivalent cation, such as cerium, or by protonation of some of the hydroxyl groups in the structure. Where phosphate completely replaces sulfate, the end members goyazite, crandallite and florencite are formed (formulae listed in Table 1). In this communication we use the abbreviation "APS" to designate solid solutions between all end-member compositions listed in Table 1.

OCCURRENCES

There are approximately two dozen published localities for svanbergite and woodhouseite (Table 2). Most of these occurrences are in intermediate-grade aluminous metamorphic rocks, in which the APS minerals are associated with quartz, pyrophyllite, andalusite, alunite, and other phosphate minerals such as lazulite and augelite (*e.g.*, Ygberg 1945, Switzer 1949, Wise 1975). The APS minerals also occur in bauxite (Shalit 1965, Bulgakova 1973), sedimentary phosphate deposits (Jiang *et al.* 1984), kaolinite claystones (Goldbery 1978) and quartz–

apatite veins (Morton 1961), though these settings are geologically unrelated to the hydrothermal environment of interest in our study.

The aluminum-rich rocks in which APS minerals generally occur are mineralogically similar to the advanced argillic assemblage (Meyer & Hemley 1967) well developed in some porphyry-copper deposits (Beane & Titley 1981), and also associated with some epithermal gold deposits and polymetallic vein systems. This alteration assemblage is characterized by extensive hydrolytic leaching of alkali cations and may contain alunite, kaolinite and diaspore in lower-temperature occurrences, or pyrophyllite, andalusite and, more rarely, corundum from higher-temperature occurrences (*e.g.*, Gustafson & Hunt 1975). The mineralogical and chemical similarity between the advanced argillic alteration assemblage and the bauxites and intermediate-grade aluminous metamorphic rocks discussed above suggests that the APS minerals might be expected to occur in association with advanced argillic alteration in hydrothermal ore deposits.

We have observed the APS minerals in three ore deposits: the Summitville gold–copper deposit (Colorado), the porphyry-copper deposit at La Escondida (Chile), and the porphyry-copper deposit at La Granja (Peru). The APS minerals occur mainly within zones of advanced argillic alteration and are generally associated with pyrite and covellite, indicative of a high fugacity of sulfur (Brimhall & Ghiorso 1983). In addition to these deposits and the localities in Table 2, we are aware of the following unpublished descriptions of hypogene APS minerals in ore deposits: svanbergite has been identified at the Golden Wonder mine in Colorado (pers. comm., P.E. Billings 1983), svanbergite occurs with uraninite, xenotime, pyrite and copper sulfides in the B.J. Lake area of the McArthur River Project, Saskatchewan (Costello 1985), woodhouseite occurs at Cerro Verde, Peru (pers. comm., E. Cedillo 1984), and Lacy (1949) observed apatite replaced by alunite "probably of a high phosphorus variety" at Cerro de Pasco, Peru.

TABLE 2. PUBLISHED OCCURRENCES OF WOODHOUSEITE AND SVANBERGITE

Location	APS Phase[1]	Associated Phases[2]	References
A. HIGH-TEMPERATURE (HYPOGENE) OCCURRENCES			
1. Champion mine, Mono County,	wd, sv	qtz, and, prl, alun, rt, numerous phosphate minerals	Lemmon (1937) Wise (1975)
2. Chizeuil, Saône-et-Loire, France	sv	qtz, and, prl, kao, dias, crn, cp, brt, cv	Lacroix (1918)
3. Circumpolar Ural Mts., USSR	sv	musc, py, carbs	Bukanov et al. (1973)
4. Dover andalusite mine, Hawthorne, Nevada, USA	sv	qtz, prl	Switzer (1949)
5. Equity silver deposit, British Columbia	sv	qtz, tour, dum, alumino-silicates, (ap)[3], hem, numerous sulfides	Cyr et al. (1984)
6. Gornyy Altai, USSR	sv	musc, (Kfs)[3]	Nikitina et al. (1965)
7. Horrsjørberg, Wermland, Norway	sv	qtz, and, prl	Ygberg (1945)
8. La Escondida, Chile	wd-sv	qtz, alun, prl, dias	This study
9. La Granja, Peru	wd	prl, and, (ap)[3] minor py	This study
10. Øldegården, S.Norway	wd	whit, qtz, (ap)[3]	Morton (1961)
11. Summitville, Colorado, USA	wd, wd-sv	alun, kao, py minor cv rare ser, ten	This study
12. Vitrefax formation, Imperial County, California, USA	sv	Sr-bar, rt, prl, kyn, tour, carn	Pemberton & Bideaux (1971)
13. Weståna, Sweden	sv	qtz, hem	Ygberg (1945)
14. Zhorga massif, USSR	sv	qtz, "hydromica", kao, py, cp, rt, topaz, brt	Sokolova & Shiryagina (1971)
B. LOW-TEMPERATURE (SUPERGENE) OCCURRENCES			
1. Andorinha-Cantahede, Portugal	sv	bauxite clay (in karst sink)	Figueiredo Gomes (1968)
2. Brunswick No. 6 mine, New Brunswick	wd	jar, pyrom, cer scor	Sabina (1967)
3. Cherkassy, USSR	sv	bauxite	Shalit (1965)
4. Ekovlevskogo, USSR	sv	?	Makarov (1967)
5. La Escondida, Chile	wd-sv	kao, "sooty chalcocite," alun	This study
6. Lebedinsk deposit, Kursk mgnetic anomaly, USSR	sv	kao, gib, hem, bauxite	Bulgakova (1973) Gladkovskii & Khramtsov (1968)
C. LESS CERTAIN ORIGIN			
1. Anhui Province, China	wd-sv	hem, qtz, cal, alun, py	Qin et al. (1984)
2. Black shales, USSR	sv	(ap)[3] crand, gor	Maulenov & Bel'skii (1970)
3. Lengóis, Bahia, Brazil	wd-sv	?	Tavora (1951)
4. Makhtesh Ramon, Negev, Israel	wd	alun, jar, kao, claystones	Goldbery (1978)
5. Novodmitrievsk Pb-Zn deposit, Donets basin, USSR	sv	py, rt	Kuznetsova et al. (1976)
6. Radjou Fe deposit, Syria	sv	hem, cal	Fijal & Niec (1977)
7. Shifang, China	sv	kao	Wu et al. (1982)
8. Szechuan, China	sv	?	Jiang et al. (1984)

TABLE 2
Footnotes

[1] wd = woodhouseite
sv = svanbergite
wd-sv = woodhouseite-svanbergite solid solution

[2] Mineral abbreviations:

alun - alunite
and - andalusite
ap - apatite
brt - barite
cal - calcite
carbs - carbonates
carn - carnotite
cer - cerusite
cp - chalcopyrite
crand - crandallite
crn - corundum
cv - covellite
dias - diaspore
dum - dumortierite
gib - gibbsite
gor - gorceixite
hem - hematite
jar - jarosite
kao - kaolinite
Kfs - K-feldspar
kyn - kyanite
musc - muscovite
prl - pyrophyllite
py - pyrite
pyrom - pyromorphite
qtz - quartz
rt - rutile
scor - scorodite
ser - sericite
Sr-bar - Strontian barite
ten - tennantite
tour - tourmaline
whit - whitlockite

[3] ( ) denotes replacement by APS mineral or cross-cutting vein relationship.

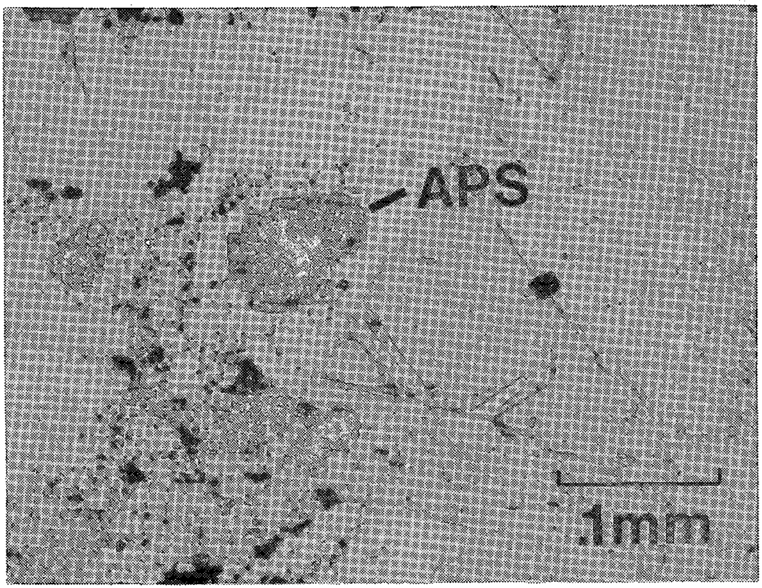

FIG. 1. Photomicrograph of APS mineral (labeled APS) enclosed in bladed alunite from Summitville, Colorado. This grain contains subequal molar proportions of calcium and strontium. Note the pseudocubic habit, which is typical of the APS minerals at Summitville.

Summitville, Colorado

Aluminum phosphate–sulfate minerals are common in the Summitville deposit, but occur in only minor amounts. They range in composition from nearly pure Sr to high-Ca varieties, and occur over a depth range of 800 metres. Hinsdalite $(Pb,Sr)Al_3(PO_4)(SO_4)(OH)_6$ also occurs locally in the deposit.

The APS minerals at Summitville occur outside the zone of most intense alteration and mineralization. This innermost zone, characterized by "vuggy silica" rock, is the result of intense hypogene acid-sulfate attack, which has removed coarse potassium feldspar phenocrysts, leaving a nearly monomineralic quartz rock crowded with coarse voids. Adjacent to this zone, a rock containing predominantly quartz and alunite, with minor kaolinite, forms a 1- to 2-metre halo, with kaolinite more abundant than alunite beyond this distance. At greater depth, kaolinite becomes more abundant or entirely supplants alunite in the interior zone of alteration around the vuggy silica (Stoffregen 1985).

APS minerals occur in the quartz–alunite and quartz–kaolinite zones at Summitville. Where associated with alunite, the APS minerals occur as 20- to 60-μm pseudocubic grains generally enclosed by alunite (Fig. 1), in nearly perfect optical continuity with the enclosing grain. In the quartz–kaolinite zone, the APS minerals occur in clusters of 10- to 30-μm pseudocubes, scattered in irregularly shaped 0.2- to 0.5-mm patches of fine-grained kaolinite. In both zones pyrite is a common accessory mineral, and covellite occurs in trace amounts. APS minerals in these two zones are rich in the svanbergite component (Sr > Ca) but show considerable compositional variability, as discussed below.

In contrast to these two types of occurrences, APS minerals close to end-member woodhouseite have been observed in one sample from a deep drill-hole at Summitville, approximately 750 metres below the main ore-zone. In this sample, the APS minerals occur as coarse blades (up to 250 μm) and are intergrown with pyrite, chalcopyrite, tennantite, and minor amounts of sphalerite containing 0.7 ± 0.1 wt.% Fe. This assemblage forms 0.5- to 1-cm veinlets that cut intensely sericitized rock.

La Granja, Peru

The APS mineral observed at La Granja is high in calcium, approaching end-member woodhouseite. It occurs in association with quartz, pyrite, pyrophyllite and andalusite. Minor amounts of apatite occur locally, and appear to have been replaced by anhedral grains (< 10 μm) of woodhouseite. Andalusite in the La Granja samples is invariably broken and enclosed in pyrophyllite mattes, strongly suggesting retrograde reaction to produce pyrophyllite from the higher-temperature andalusite-bearing assemblage. The woodhouseite grains occur in contact with pyrophyllite, and the two phases are interpreted to have formed in equilibrium based on this textural criterion.

La Escondida, Chile

At La Escondida, APS minerals are probably of both hypogene and supergene origin. The probable hypogene occurrence consists of grains 5 to 50 μm in size, intermediate in composition between svanbergite and woodhouseite, and intergrown with diaspore. An extensive zone of hypogene alunite–pyrophyllite–diaspore alteration is spatially associated with the APS minerals on a broad scale (Brimhall *et al.* 1985, Alpers 1986), but no grain contacts between pyrophyllite or alunite and the APS minerals have been observed.

In contrast, several finer-grained occurrences of APS minerals at La Escondida are considered to be of supergene origin. In drill intercepts in the leached capping zone, cryptocrystalline material intermediate in composition between woodhouseite and svanbergite fills late fractures and occupies more than 30% of some fist-sized core samples. Fine-grained APS minerals in the zone of supergene copper enrichment are spatially associated with supergene copper sulfides (mainly "sooty chalcocite", a fine-grained mixture of djurleite, digenite and anilite: Alpers 1986), which rim and replace hypogene sulfide grains.

CHEMICAL COMPOSITION

Woodhouseite and svanbergite have been chemically analyzed with the ARL 8-channel electron microprobe at the University of California, Berkeley. An accelerating voltage of 15 kV was used, with sample current ranging from 0.012 to 0.022 microamperes. Standards included Marysvale alunite, natural brazilianite, and synthetic anhydrite, celestite and barite. A diffuse beam (10 to 30 μm in diameter) was used to analyze all alunite samples and standards to minimize problems with vaporization of sodium and potassium.

Table 3 lists average compositions of three APS grains from the Summitville deposit, and one grain each from La Granja and La Escondida. Most of these grains show variation in calcium and strontium contents of from 0.1 to 0.2 formula units. Molar ratios of phosphate to sulfate are nearly constant in most grains, and range from a minimum value of 1:1, the expected value for stoichiometric woodhouseite or svanbergite (Table 1), to a maximum of 1.5:0.5, observed in some Summitville samples.

TABLE 3. COMPOSITIONS OF ALUMINUM PHOSPHATE-SULFATE MINERALS

	1	2	3	4	5
K_2O	.12	n.d	1.00	n.d.	.21
Na_2O	n.d.	n.d	.11	n.d.	n.d.
CaO	6.08	3.74	10.18	9.65	3.08
SrO	9.70	15.79	2.44	5.75	15.24
BaO	.90	.28	2.56	1.14	.50
Ce_2O_3	.40	n.d.	n.d.	n.a.	.13
Al_2O_3	35.24	34.43	35.87	35.79	34.37
SO_3	10.19	11.08	16.27	17.60	16.63
P_2O_5	23.25	22.25	18.41	17.91	17.06
H_2O 1/	13.50	12.80	13.10	12.90	12.30
Total	99.38	100.38	99.94	100.74	99.52
K	.014	n.d.	.091	n.d.	.019
Na	n.d.	n.d.	.014	n.d.	n.d.
Ca	.473	.297	.776	.729	.245
Sr	.408	.678	.100	.235	.656
Ba	.026	.008	.070	.031	.015
Ce	.020	n.d.	.002	n.a.	.007
Al	3.014	3.005	3.010	2.975	3.009
S	.555	.616	.869	.932	.927
P	1.432	1.398	1.110	1.072	1.076
OH 2/	6.535	6.320	6.200	6.019	6.092

1/ weight % H_2O calculated based on observed values of calcium, strontium, phosphorus, and sulfur (see text).
2/ moles OH calculated based on weight % H_2O above.

Description of samples.

1. Summitville sample 266-273, elevation 3544 m.
2. Summitville sample 281-401, elevation 3553 m.
3. Summitville sample 14-2547, elevation 2827 m.
4. La Granja sample 6-120; DDH-6, 120 m. depth
5. La Escondida sample 1067-C-159; DDH-97, 278 m. depth.

n.d. = not detected; detection limit is estimated at .05 weight % oxide component.
n.a. = not analyzed for.

Compositional variations in the molar ratios PO_4^{3-}/SO_4^{2-} and Ca^{2+}/Sr^{2+} from selected Summitville and La Escondida samples are illustrated in Figure 2. This plot does not take into account the presence of Ba^{2+} and Ce^{3+}, which are significant in the samples from La Granja and some of the samples from Summitville.

The deeper samples at Summitville (*e.g.*, sample 3, Table 3) are from a part of the deposit in which pyrophyllite is locally abundant, suggesting a higher-temperature origin than for the shallower APS minerals, which are accompanied by alunite and kaolinite. The La Granja samples (*e.g.*, sample 4, Table 3) occur with abundant pyrophyllite and thus are likely to represent a higher-temperature occurrence as well. These samples show distinct chemical differences from the inferred lower-temperature samples, including higher contents of calcium (some samples approach end-member woodhouseite), and high barium contents, with a maximum of 9.58 wt.% BaO in one sample from La Granja. The deep APS minerals at Summitville are also noteworthy in containing appreciable potassium, suggesting an increase in the extent of solid solution between the APS minerals and alunite at higher temperature.

Cerium occurs in trace amount in some samples, to a maximum value of 3.59 wt.% Ce_2O_3 noted in a shallow occurrence at Summitville that has roughly

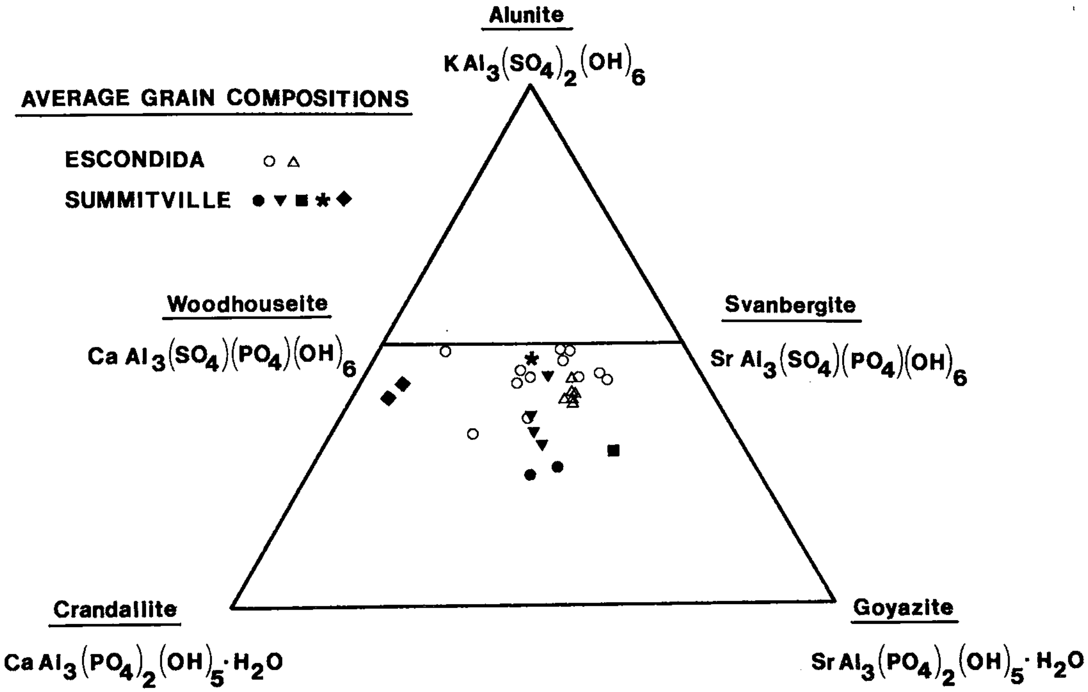

FIG. 2. Compositional data on APS minerals from Summitville (solid symbols) and La Escondida (open symbols). Individual symbols represent average compositions for single grains. Grains from within the same thin section all have the same symbol.

equimolar Ca^{2+} and Sr^{2+}. Other *LREE* are probably present in small amounts in these phases, as indicated by whole-rock X-ray-fluorescence data on La Escondida samples containing abundant APS minerals; neodymium and praseodymium values are up to 25 times background levels. Qualitative analysis by electron microprobe indicates that lead and arsenic contents are low to negligible in woodhouseite–svanbergite solid solutions from all three localities studied.

The H_2O contents listed in Table 2 were computed using the observed molar ratios of Sr^{2+} to Ca^{2+} and of PO_4^{3-} to SO_4^{2-}. APS minerals with high Ca^{2+} have relatively high water contents by weight owing to the lower molecular weight of Ca^{2+} compared with Sr^{2+}. Phosphate in excess of one mole per formula unit also increases water content, because the additional negative charge created by this increase is assumed to be balanced by the addition of H^+. This implies that the amount of H_2O per formula unit should equal the amount of phosphate in excess of 1 mole per formula unit, neglecting the influence of cerium. This relation is expressed by the general formula $RAl_3(PO_4)_{1+x}(SO_4)_{1-x}(OH)_{6-x} \cdot (H_2O)_x$, which is approximately followed in all the compositions listed in Table 3.

MISCIBILITY BETWEEN THE APS MINERALS AND ALUNITE

Another point to be addressed is the extent of solid solution between the APS minerals and alunite. Although whole-rock compositions indicate that alunite may contain appreciable phosphorus, strontium, and lesser calcium (*e.g.*, Schrader 1913, Frondel 1958, Kashkai 1970), these data are not reliable because they may reflect the presence of APS grains within the analyzed samples. Significant solid-solution between APS minerals and alunite has been documented by Wise (1975), who observed a "strontian natroalunite" with 25 mole % PO_4^{3-}, in substitution for SO^{2-} and a similar amount of Sr^{2+} for Na^+. In addition, natroalunite with up to 18 mole % calcium and significant phosphate has been reported from South Africa (Schoch *et al.* 1985, in prep.).

In contrast to these appreciable substitutions in natroalunite, the alunite from Summitville shows low phosphate, calcium, and strontium contents (sample 1, Table 4). Alunite from La Escondida is somewhat richer in phosphorus and strontium than the Summitville samples (sample 2, Table 4). It is interesting to note that the molar amount of PO_4^{3-}

TABLE 4. CHEMICAL COMPOSITION OF ALUNITE

	1	2	3	4	5
K_2O	7.49	9.18	10.79	10.84	9.66
Na_2O	2.41	1.44	n.d.	.19	1.04
CaO	n.d.	n.d.	n.d.	n.d.	.05
SrO	.05	.34	.38	.31	n.d.
BaO	n.a.	n.d.	n.d.	n.d.	.20
Al_2O_3	37.34	36.80	36.70	36.92	37.13
SO_3	38.44	38.67	37.07	36.94	37.96
P_2O_5	.23	.30	.63	.86	.05
H_2O 1/	13.20	13.05	13.05	13.05	13.10
Total	99.16	99.78	98.62	99.11	99.19
K	.656	.805	.961	.952	.853
Na	.321	.192	n.d.	.024	.139
Ca	n.d.	n.d.	n.d.	n.d.	.003
Sr	.002	.014	.016	.012	n.d.
Ba	n.a.	n.d.	n.d.	n.d.	.005
Al	3.017	2.980	3.021	2.998	3.029
S	1.978	1.994	1.944	1.91	1.975
P	.013	.018	.036	.049	.002
OH 2/	6.048	5.981	6.080	6.003	6.034

1/ weight % H_2O calculated as in Table 2.
2/ moles OH calculated as in Table 2.

Description of samples.

1. Summitville alunite 255-629.
2. Escondida alunite 1067-C-298.
3. La Tolfa alunite.
4. Marysvale alunite.
5. Goldfield alunite.

n.d. = not detected; detection limits as in Table 2.
n.a. = not analyzed for.

in these samples, as well as in other analyzed samples of alunite, exceeds in all cases the molar Sr^{2+} + Ca^{2+} content. This leaves uncompensated some of the additional negative charge introduced by the phosphate substitution. This discrepancy may be explained by the presence of minor amounts of other cations in the *R* site (*e.g.*, Pb^{2+}), or perhaps by the protonation of some hydroxyl groups in the alunite.

To provide a basis of comparison for these results, we have also analyzed alunite from three other localities: La Tolfa (Italy), Marysvale (Utah) and Goldfield (Nevada). Of these, the first two are believed to have formed at or near the surface, not directly related to precious metal mineralization (Lombardi & Barbieri 1983, Cunningham *et al.* 1984), whereas the third is a gold–sulfosalt deposit similar to Summitville (Ashley 1974). We have not detected APS minerals in any of these samples. However, the La Tolfa and Marysvale alunite has significant and fairly consistent SrO and P_2O_5 contents (samples 3 and 4, Table 4). These compositional data are similar to whole-rock chemical data on monomineralic alunite rock from both La Tolfa and Marysvale (pers. comm., C.G. Cunningham 1984, Lombardi & Barbieri 1983) and indicate that the whole rock SrO and P_2O_5 values probably reflect the presence of these elements in alunite. Goldfield alunite (sample 5, Table 4) contains up to 0.2 wt.% BaO but no detectable strontium and only 0.05 wt.% P_2O_5.

The substitution of Sr and Ca into alunite and the occurrence of strontium-bearing APS minerals within the advanced argillic zone have important implications for patterns of whole-rock abundance of elements developed around hydrothermal ore deposits. Such patterns are commonly used in exploration for base and precious metal deposits (*e.g.*, Govett 1983). In particular, the Rb/Sr and K/Ca ratios are profoundly altered within the zone of advanced argillic alteration relative to patterns observed in the potassic, phyllic and propylitic zones (Schwartz 1982, Alpers & Stoffregen, in prep.).

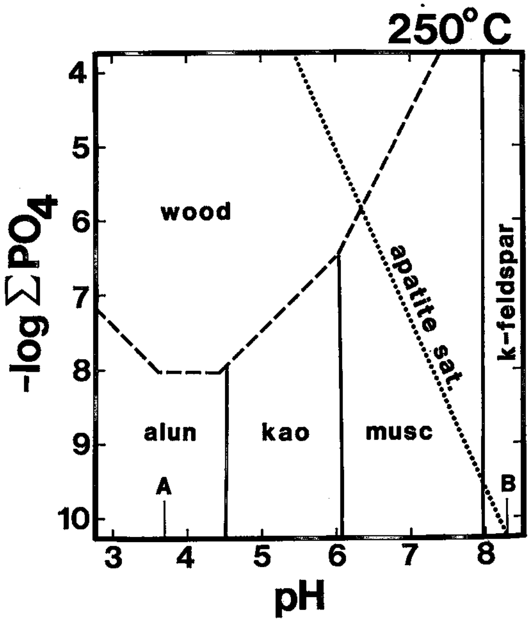

FIG. 3. Plot of stability fields of selected alteration minerals in the system $CaO–K_2O–Al_2O_3–SiO_2–SO_3–P_2O_5–H_2O$ in terms of pH and total dissolved phosphate at 250°C and 40 bars (vapor saturation). The pH boundaries between alunite, kaolinite, muscovite and potassium feldspar in the presence of quartz are computed using data from Helgeson *et al.* (1978) and assuming a log total potassium molality of –3.0, and a log total sulfate molality of –1.5. The apatite saturation-line and the pH dependence of H_3PO_4 dissociation are computed using data from Barner & Scheuerman (1978), Wolery (1983) and Vieillard & Tardy (1985), and an assumed log total calcium molality of –5.0. Line A indicates the pH for equal activities of $H_3PO_4^-$ and $H_2PO_4^-$; line B represents the pH value for equal activities of $H_2PO_4^-$ and HPO_4^{2-}. An approximate lower bound on woodhouseite stability is indicated by the short dashed lines. In constructing this boundary, provision was made for complexing of calcium and potassium with sulfate, using data from Wolery (1983). The location of this boundary relative to the other fields shown on the figure is inferred from observed natural assemblages, as discussed in the text.

PARAGENESIS AND CONDITIONS OF FORMATION

APS minerals are believed to form by replacement of apatite, or in response to apatite dissolution, in the low-pH environment that characterizes advanced argillic alteration. An antipathetic relationship between apatite and the APS phases is particularly well illustrated in the Summitville deposit. Here primary apatite is common as an accessory phase in the fresh host-rock, where it occurs in euhedral prismatic grains up to 2 mm in length. These apatite grains also occur in the distal, montmorillonite-dominated zone of clay alteration around the vuggy silica zone, and locally in the adjacent illitic alteration zone. Apatite is absent from the more proximal quartz–kaolinite and quartz–alunite zones, as well as the vuggy silica alteration zone. As noted above, the APS minerals occur in the quartz–kaolinite and quartz–alunite zones, as well as in association with intense sericitic alteration at greater depths in the deposit. APS minerals have not been noted in association with illitic or montmorillonitic alteration at Summitville.

These observations, together with thermodynamic data on hydroxyapatite, alunite, kaolinite, muscovite, potassium feldspar and various aqueous complexes, are used to construct a diagram showing the inferred field of stability of woodhouseite as a function of pH and total dissolved phosphate (Fig. 3). This diagram pertains to a temperature of 250°C, the estimated temperature of vein mineralization in the upper part of the Summitville deposit (Stoffregen 1985), and to the vapor-saturation pressure at this temperature (40 bars). The pH boundaries between alteration minerals are computed using a log total potassium molality of -3.0, and a log total sulfate molality of -1.5. The apatite field is bounded by the apatite-dissolution reaction

$$Ca_5(PO_4)_3(OH) + 7H^+ = 5\,Ca^{2+} + 3\,H_2PO_4^- + H_2O \qquad (2)$$

assuming a log total calcium molality of -5.0. Although the potential effects of fluoride and chloride on apatite stability are not considered, Figure 3 nevertheless provides a useful representation of the observed natural assemblages.

No thermodynamic data exist for woodhouseite or svanbergite at any temperature. However, some general constraints can be placed on the stability field of the APS minerals based on the petrological observations described above. This is illustrated by the dashed line on Figure 3, which provides an approximate stability-boundary for woodhouseite in terms of total dissolved phosphate and pH. Figure 3 indicates that woodhouseite can coexist with alunite or kaolinite or both, in accord with the assemblages described above, and also with muscovite, as is suggested by the association of woodhouseite with sericitic alteration at depth in the Summitville deposit.

Figure 3 also indicates that apatite may coexist with muscovite, in agreement with the association of apatite with illitic alteration at Summitville and also with the reported association of apatite with muscovite in vein mineralization at Panasqueira, Portugal (Kelly & Rye 1979). However, apatite cannot coexist with kaolinite or alunite for the conditions assumed in Figure 3. This is in accord with the observed replacement or dissolution of apatite that has accompanied advanced argillic alteration in the deposits studied.

The replacement of apatite by APS minerals in the pyrophyllite zone at La Granja suggests that similar arguments apply at somewhat higher temperatures. Based on data from Hemley *et al.* (1980) on the system Al_2O_3–SiO_2–H_2O, the pyrophyllite-bearing assemblage at La Granja probably formed between 260 and 350°C. The paucity of alunite in this deposit (Schwartz 1982) may also reflect a somewhat higher temperature of alteration (*cf.* Hemley *et al.* 1969).

SUMMARY AND CONCLUSION

Aluminum phosphate–sulfate minerals that are isostructural with alunite but contain Sr^{2+} and Ca^{2+} in place of K^+ and Na^+ have been reported from approximately two dozen localities to date. Previously described occurrences are mainly in aluminum-rich intermediate-grade metamorphic rocks. This report describes three new occurrences of these "APS" minerals, two from porphyry-copper deposits (La Escondida, Chile and La Granja, Peru), and one from a lode gold – quartz – alunite deposit (Summitville, Colorado). In all three occurrences, the APS minerals occur within zones of advanced argillic alteration; at both Summitville and La Escondida this includes abundant kaolinite, alunite, and locally abundant pyrophyllite, whereas at La Granja, pyrophyllite and andalusite are common, but alunite is rare.

An APS component occurs in alunite from both the Summitville and La Escondida deposits, and also in alunite from Marysvale and La Tolfa. SrO values of 0.10 to 0.30 wt.%, and P_2O_5 values of 0.30 to 0.60 wt.% are common in these samples, and maximum values of 1.12 wt.% SrO and 2.41 wt.% P_2O_5 have been observed in a sample of alunite from La Escondida. This is in contrast to the more extensive solid-solution of natroalunite with APS minerals in higher-temperature andalusite- and sillimanite-bearing assemblages reported by Wise (1975) and Schoch *et al.* (1985, in prep.).

APS minerals occur in trace amounts in all three deposits studied in this report. Their lack of distinctive optical properties suggests that they may have been overlooked in other deposits containing advanced argillic alteration, particularly those with apatite-bearing host rocks. Our observations indicate that apatite is unstable in this setting, and is either dissolved or replaced by the APS minerals. This is in accord with existing thermodyamic data on apatite stability at 250°C.

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