Stypteria phorime as alunogen in solution: Possible pointer to the gradual cooling of the Melos geothermal system*

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ABSTRACT: We report here the nature of alum from Melos described in classical and later sources, and reconfirm that it was predominantly the mineral alunogen, $Al_2(SO_4)_3.17(H_2O)$. Given that some sources report in addition to solid alum the presence of 'liquid' alum, as the most abundant form of alum, (*stypteria phorime),* and that this is presently scarce, we suggest that its scarcity may be corroborating evidence for cooling of the Melos geothermal field.
Key-words: *alum*, *geothermal system, Melos*.

ΠΕΡΊΛΗΨΗ: Στην παρούσα εργασία μελετάται η φύση της στυπτηρίας της Μήλου που περιγράφεται στους Κλασσικούς χρόνους και μεταγενέστερα και αντιπροσωπεύεται κυρίως από το ορυκτό αλουνογενής. Μερικές αρχαίες πηγές σημειώνουν ότι αν και υπήρχε «ξηρός» αλουνογενής, το μεγαλύτερο ποσοστό του ορυκτού αυτού αναπτύσσονταν με την έφυγρη μορφή του, αν και σήμερα συμβαίνει το αντίθετο. Υποθέτουμε ότι αυτό το φαινόμενο πιθανά να σχετίζεται με την ψύξη του γεωθερμικού πεδίου της Μήλου.
Λέξεις-κλειδιά: *στυπτηρία, γεωθερμικό σύστημα, Μήλος.*

INTRODUCTION

Tu-ru-pte-ri-ya (in Linear B*), stypteria* (in Greek*),*and *alumen* (in Latin*),* as well as *stypteria phorime*, *paraphoron, stroggyle* and *schiste* are some of the names given to 'alum' in the works of authors such as Dioscorides, Pliny and Galen It was not until the late 19th century that the mineralogical nature of these substances was investigated. They are now all considered to be alum group minerals, i.e. hydrated aluminium sulphates. This however still leaves us with the question: which were precisely the alum mineral(s) of Melos described in some detail by some writers of antiquity and travellers to the island in the 15th-19th centuries; and what about 'liquid' alum (*stypteria phorime)* a rather unexpected observation not only for a mineral but an abundant one as well.

The detailed mineralogical study and stable isotope investigation reported in Hall *et al.* (2003a) led us to conclude that the Melian *alumen* of Pliny was mainly alunogen, i.e. aluminium sulphate hydrate that is commonly found associated with fumaroles and is derived by acid sulphate alteration of rocks.

In Hall & Photos-Jones (2009) we tackled the issue of *paraphoron* and *phorimon;* we concluded that the most common variety of solid *alumen* on Melos was not K-alum, as might have been expected, but rather alunogen, an aluminium sulphate hydrate; also that 'liquid' *alumen (phorimon*) could have been a gel-like form of alunogen/aluminium sulphate, which we produced experimentally through heating and cooling of an alunogen solution; this was done in the process of demonstrating how the natural *alumen* of Melos could be purified by physical and chemical processing. In Hall & Photos-Jones (2009) we therefore took 'liquid' to mean gel-like (amorphous).

In this paper we corroborate the arguments raised above regarding natural and processed *alumen,* but furthermore suggest that 'liquid' alunogen may have been found on Melos in the past in its natural dissolved state, as suggested by the classical and later sources and that the reason that it is not evident today is on account of diminishing geothermal activity. We argue that *phorimon* may have been a saturated solution of alunogen 'dripping' out from fissures within caves or around open air fumaroles where it may have accumulated in pools.

Evidence for open air pools would have been more difficult to establish, compared to similar pools within caves, since alunogen-rich solutions in open air would have easily evaporated leaving behind an alunogen-rich crust. Indeed such dried up pools identified by their high alunogen content have been observed at a number of places (Photos-Jones & Hall, in prep.). The alunogen in dried up pools may have also end up in a gel-like form.

In summary we suggest that the *alumen* of the Classical and Roman periods was fumarolic alum - primarily the mineral alunogen -which was 'harvested' rather than mined or quarried in antiquity and in later periods; liquid 'alum' was probably alunogen in solution which has almost disappeared from Melos possibly on account of the geothermal energy gradually diminishing; the quantity of alunogen found around fumaroles today is probably much less now than in the past.

* *Stypteria phorime* ως έφυγρος αλουνογενής: Πιθανός δείκτης βαθμιαίας ψύξης του γεωθερμικού συστήματος της Μήλου

THE NATURE AND PROPERTIES OF *STYPTERIA/ALUMEN*

The alum group minerals are industrial minerals, which were recovered in antiquity from the island of Melos, in the SW Cyclades (Figs 1, 2). Industrial minerals are inorganic materials that are usually natural earth resources. In the Classical and Roman periods, some Aegean industrial minerals were known as '*earths*' (*γαίες)* and usually named after the place where they came from (Photos-Jones *et al.,* 1999; Hall & Photos-Jones, 2009). It can be difficult enough defining and explaining modern industrial minerals but, in the case of 'earths', this is even more problematic particularly since their identification rests on properties and uses, and more than one substance shared the same properties.

One of the major properties of alum is its astringency and this allusion to astringency has been inherited by the nomenclature so that words that we assume to mean, or relate to, 'alum' tend to imply 'astringency'. However, not only alum group minerals are astringent, metal salts like ferric sulphate (χαλκίτις), or vegetable substances share the same property. So research into alum group minerals also involves how astringents were perceived both as a taste sensation as well as an indicator of a medicinal property (Photos-Jones & Hall, in press).

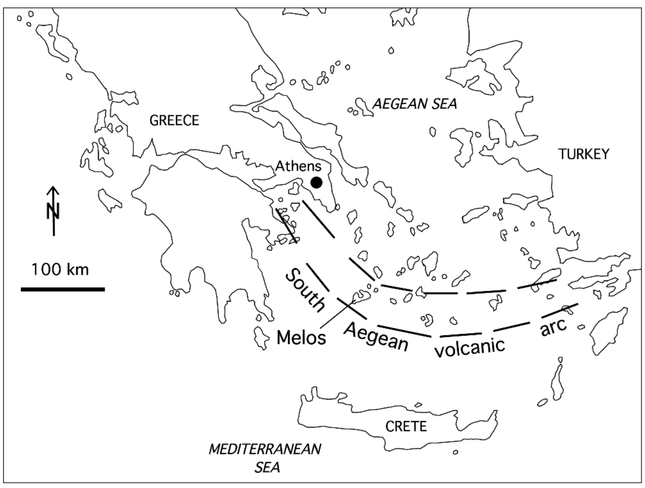


Fig. 1. Map of Greece and the Aegean showing the location of Melos in the South Aegean volcanic arc. The dashed lines indicate the approximate boundaries of the volcanic arc.

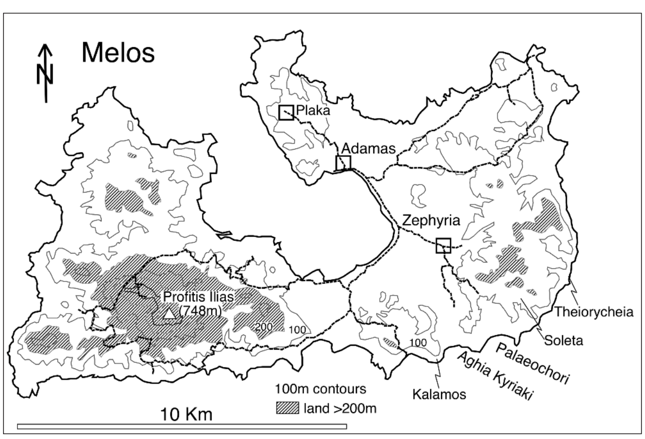


Fig. 2. Melos: simplified topographic map. The island is quite hilly in the east, yet the highest and most rugged terrain is in the south-west. The map shows the main modern settlements (squares), main roads, and places mentioned in the text.

Contrary to ancient sources, modern medical research does not appear to be interested in alum, which is likely to be a bacteriocide when used in deodorants for example, but we do not have any sound scientific references to support its antibacterial properties. It has long been used in styptic sticks. It seems likely that alum's astringency is due to the coagulation of organic molecules such as proteins and this property would probably suffice to give the medicinal benefits to Pliny's *alumen*

The properties of alum that led to its use as a mordant have been well-considered. It is most likely that the small highly charged Al^{3+} cation binds the complex dye molecules to those of the fibre. The electronic modification of the new metallo-organic site can enhance the dye colour (Delamre & Monasse, 2009). Ferric iron (Fe^{3+}) can also be used as a mordant but it tends to darken dye colours (Cardon, 2003).

Well before the reference to *stypteria* (*alumen*), by Dioscorides (De *Material Medica*, Book V, 123) in the first century AD, this astringent material was mentioned for the first time, as *tu-ru-pte-ri-ja*, in four Linear B clay tablets, dating to the Late Bronze Age c. 1000-1200 BC. Two of the clay tablets originate from Pylos, PY An35 and PY Un443 and one is from Tiryns TI X 6; a fourth one is from Knossos, KN X 986 where it is listed as *tu-ru-pe-te* (Bennett & Olivier, 1973; Perna, 2005). In the Pylos Tablets, *tu-ru-pte-ri-ja* is mentioned in association with two blacksmiths, *ku-pi-ri-jo (*PY Un 443) and *a-ta-ro (*PY An35) who received goods like wool in exchange for alum (Perna, 2005). Firth (2007) suggested that the alum referred to in these tablets was probably 'alum-stone', which he equates with alunite, which was roasted in the fires of the blacksmiths to be converted to alum, and used as a mordant. Very little can be deduced from these enigmatic references in the Linear B tablets other than the fact that this subtances was not only known but also an item of trade.

Dioscorides gives an account of the medicinal applications of *stypteria*: 'for medicinal purposes use the *schiste*, *stronggyle* and the liquid one. *Schiste* is the best' (Dioscorides *De Materia Medica* Book V, 123) (προς δε ιατρικήν χρήσιν λαμβάνεται η σχιστή τε και η στρογγύλη και η υγρά) (Kuhn 1829, 788); However, in the English translation by Gunther (1934, 643), based on an earlier translation dated 1655 by Goodyear, the same passage reads as 'but for medicinal use, both ye Scissilis, and the Round, and ye Moist is taken; but ye Scissilis is the best'

In reference to '(στυπτηρία) υγρά', the words 'liquid' and 'moist' are given which reflect two non-identical physical states, although both clearly suggest that the said type of alum was not solid. Galen writes that liquid alum was called *phorimon (*meaning bearing fruit) because it was abundant (Lev-

IDIS, 1994, 477). Since antiquity, commentators and translators have added their own 'interpretation' to the original texts, so it is perhaps 'safer' to look at both the original - be it in Greek or Latin - as well as that provided by the translation.

Apart from discussing the medicinal uses of *alumen*, Pliny (*Natural History* Book 35, 52) provided information on the nature of the substance. [translation of BOSTOCK & RILEY (1857) in BAILEY (1932)]: *'Every kind of alumen is a compound of slime and water, or in other words, it is a liquid product exuding from the earth; the concretion of it commences in winter, and being completed by the action of the summer sun.....*" We can take this as a clue to the soluble nature of *alumen* and its likely appearance on the surface of the earth near a feature like a fumarole. There is little doubt that Melian *alumen* was divided into two groups, solid and liquid; the main prerequisite for the quality of liquid *alumen* is to be clean, milky, not to grind when rubbed between the fingers (Pliny, *Natural History* Book 35, 52); liquid *alumen* is astringent.

ALUNITE IN MELOS

Alunite, $KAl_3(SO_4)_2(OH)_6$, is a potential ore of alum but it requires roasting and slaking to produce alum in solution. The chemical process requires a change in ratios of components and removal of Al^{+++} presumably as an insoluble aluminium hydroxide as shown in the following reaction (HALL *et al.*, 2003a):

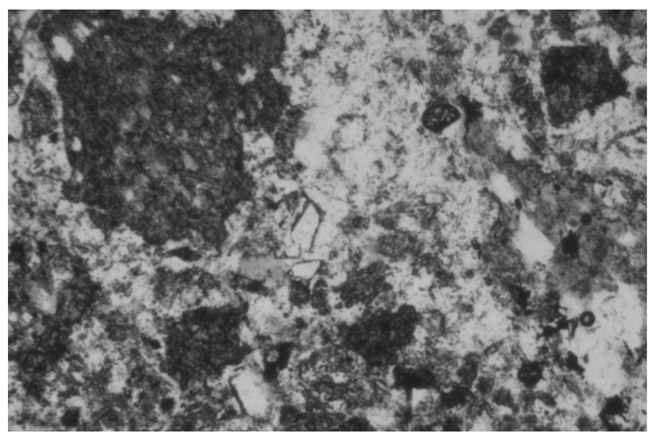
$$\underset{\text{alunite}}{KAl_3(SO_4)_2(OH)_6} + 12H_2O \longrightarrow \underset{\text{K-alum}}{KAl(SO_4)_2.12H_2O} + 2Al(OH)_3$$

It has been argued that alunite processing was not developed until the medieval period (SINGER, 1948; CARDON, 2003) when the main use of alum throughout Europe was as a mordant for fixing dyes to vegetable fibres; However, archaeological evidence for alunite processing in antiquity is present in the island of Lesvos, in the North Aegean and dates to the Roman period (ARCHONTIDOU, 2005).

Alunite extraction and processing in Melos for the purpose of manufacturing alum has, at best, been elusive. As consecutive surveys have shown (MCNULTY, 2000; PHOTOS-JONES *et al.,* 1999; PHOTOS-JONES & HALL, in prep.) there has been no clear evidence for kiln structures with associated alum waste. The ceramic wasters from one possible kiln site, at Soleta (Fig. 2), to the NE of Aghia Kyriaki bay, are thought to be pottery kiln wasters rather than alum related ones (PHOTOS-JONES & HALL, in prep.). However, alunite is widespread in SE Melos.

Alunite-bearing samples located during our investigation of the SE Melos area were of pervasively altered rocks (Fig. 3) and are presumed to be the result of relatively early and relatively high temperature hydrothermal alteration. Alunite is a typical product of acid sulphate alteration (KELEPERTSIS, 1989), in particular of K-feldspar and it can form over a large temperature range (NORDSTROM, 1982). Alunite is difficult to identify in the field but as well as being confirmed using X-ray diffraction alunite was seen in thin section to occur in the matrix of 'ghost' breccia samples (Figs 4a, b). Acid sulphate alteration requires fluids rich in sulphuric acid and in the volcanic setting of SE Melos this would have been provided by

Fig. 3. Photograph of altered 'white rock' that typically contains alunite.In this case the rock has formed by acid sulphate aleration of a metamorphic breccia.



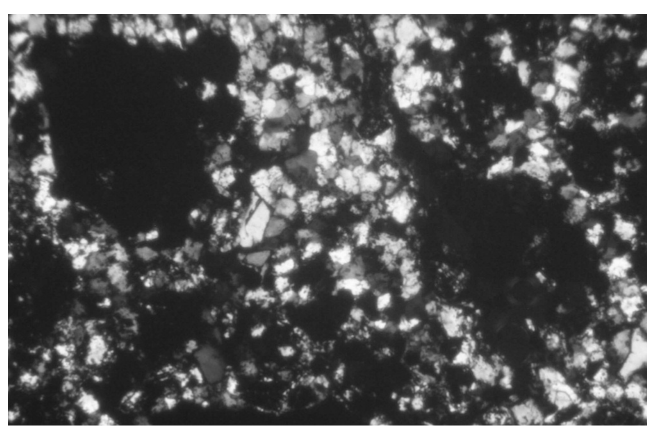


Fig. 4a. Alunite in thin section (ppl); the transparent and colourless areas contain alunite.
Fig. 4b. Alunite in thin section (xpols) the abundant crystals showing light grey interfrence colours are mainly alunite. Same view as in Figure 4a.

oxidation of hydrogen sulphide or other sulphur species presumed to have originated from magmas. Sulphur isotope values of all sulphur-bearing minerals related to geothermal activity on Melos, are consistent with this scenario (HALL *et al.,* 2003a).

MELIAN *STYPTERIA/ALUMEN*: ALUNOGEN AND SULPHUROUS FUMAROLES

Melian *stypteria/alumen* is most likely to have been an aluminium sulphate salt with added impurites from additional sulphates. Most of the diverse industrial minerals from Melos are related to the island's volcanism and unusual altered 'white rock' which testifies to the island's continuing albeit declining geothermal activity. By 'white rock' we imply the hydrothermal alteration product of rocks which form the island's bedrock. 'White rock' is to be found typically under alluvial sediment or under recent bedded volcanic tuffs which in turn are overlain by alluvial sediment (HALL *et al.,* 2003a).

While deeper geothermal processes (Fig. 5) have produced industrial minerals like kaolin and bentonite, surface manifestations of geothermal activity such as fumaroles give rise to minerals like sulphur and alum, the latter often occurring as efflorescences in the vicinity of sulphurous fumaroles. There are currently only a few active fumaroles, yet fumaroles have been active throughout the human occupation of the island. Fumaroles are renewable sources of natural materials and their exploitation would have been ongoing hence our suggestion that alum could have been 'harvested'.

When trying to establish the nature of Pliny's Melian *'alumen*', the first task is to locate and understand the origin of potential deposits of alum. All occurrences of white mineral precipitates such as cavern wall efflorescences were investigated and samples usually identified using powder x-ray diffraction. Crystalline growths were commonly gypsum but

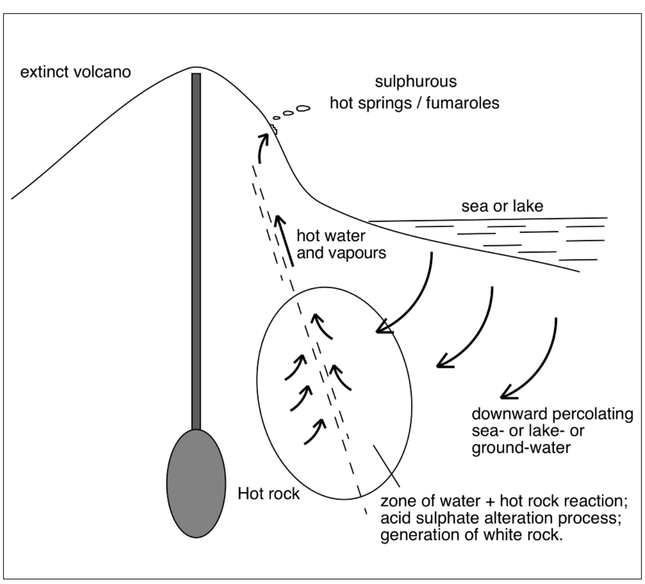


Fig. 5. General model illustrating acid-sulphate rock alteration and the formation of altered 'white rock'.

epsomite, halite and alunogen were also located. Eventually it was discovered that the most dependable locality for alum was adjacent to fumaroles albeit sub-aerially or underground. Although Melos is well known for its offshore submarine 'fumaroles' (CRONAN & VARNAVAS, 1993; DANDO *et al.,* 1995; VALSAMI-JONES *et al.,* 2005), there is little prospect of alum being found here, as it is so soluble.

Fig 6 demonstrates how alum (alunogen) may be formed at sulphurous fumaroles. The sulphur comes from depth and has an ultimate magmatic origin (confirmed by sulphur isotope analysis, HALL *et al.,* 2003a). It is likely that that the main sulphurous gas leaving magma is H_2S but this can be oxidised *en route* upwards producing native sulphur. Eventually native sulphur forms at the mouths of small fumaroles and accumulates in the ground around fumaroles. Such sulphur is weathered and oxidised producing sulphuric acid which, on sinking downwards can attack rock and produce alum. Sulphuric acid can also be produced deeper in the system and the acidic solution attack rock to produce white rock at depth (Fig. 5). So white rock, with alunite, may be produced by acidic sulphate alteration in several ways and alunogen would be one of the soluble by-products. Alunogen can therefore be in solution when it reaches the surface near fumaroles.

When fumaroles come out of the ground, the vapour must contain sulphur and water. Any H_2S in the vapour would be in the process of getting oxidised to sulphur and/or sulphur dioxide. Native sulphur grows by sublimation from vapour at the mouth of fumaroles because the vapour is cooling rapidly as it leaves the fumarole mouth. Water in the vapour coming from fumaroles may produce steam so it is forming liquid water due to cooling. This is condensation.

So there are two parallel processes taking place at the mouth of the fumarole: alunogen efflorescence and sulphur sublimation. Alunogen grows as efflorescences around fumaroles because aluminium-saturated solutions reach the surface near fumaroles and water evaporates while dissolved aluminiuim sulphate crystallises as growths of alunogen. Other metals may follow aluminium, but many, including iron, will be travelling in solution away from the main alteration zone. We know this because of red-stained rock around white alteration zones. This is explained by oxidation of ferrous iron to insoluble ferric iron oxyhydroxides once it has migrated some distance away from the zone of altertation. Manganese is likely to follow iron.

Any rainwater or steam condensate has the potential to dissolve alunogen and cause the aluminiuim sulphate to either be transported away from the fumaroles or sink to depth and be recycled. Runoff from fumarole areas will contain much dissolved aluminium sulphate. If this is ponded and evaporated, then alunogen is likely to be the main phase formed. Alunogen can therefore form in many ways around fumaroles. Figs 7a and 7b illustrate the occurrence of white alum minerals, mainly alunogen in the solfatara zone at Aghia Kyriaki, as well as sulphur sublimates.

DIMINISHING GEOTHERMAL ACTIVITY: THE SEDIMENTS

There are indications that the geothermal gradient was higher in the past: reddening of alluvial sediments associated with Roman occupation of the Aghia Kyriaki site is widespread in places and has led us to suggest that 'hot ground' could have been used as a heat-source in antiquity for mineral processing (PHOTOS-JONES *et al*., 1999). Excavation would help determine the relative age of ground heating and archaeological features such as buried pots and walls at Aghia Kyriaki and West Palaeochori. (Fig. 8) Steam-rooms and spas were popular on Melos in the Middle Ages (e.g. GRASSETTO, 1511) but they were declining by the 1780s (SUTHERLAND, 1790) and no longer feature prominently on Melos where the evidence for their presence is gradually disappearing.

Phreatic explosion craters have been reported in the SE part of the island (Aghioi Theodoroi, Soleta) and there are archaeological remains (pottery and glass) trapped within the debris of these explosions (PHOTOS-JONES & HALL, in prep.). From detailed geological mapping (PHOTOS-JONES *et al.,* 1999), the most recent volcanism at Fyriplaka on Melos is clearly pre-occupation of the Aghia Kyriaki site consistent with the 100 Ka date for the youngest volcanism on Melos, provided by FYTIKAS (1977).

'HARVESTING' OF ALUM FROM SULPHUROUS FUMAROLES IN CAVES/MINES: THE SOURCES

Important documentary evidence of the exploitation of Melian alum is provided by Tournefort, a traveller and natural historian of the early 18th century who visited the Cyclades and Melos in particular in 1700. He describes his visit to an alum 'mine':

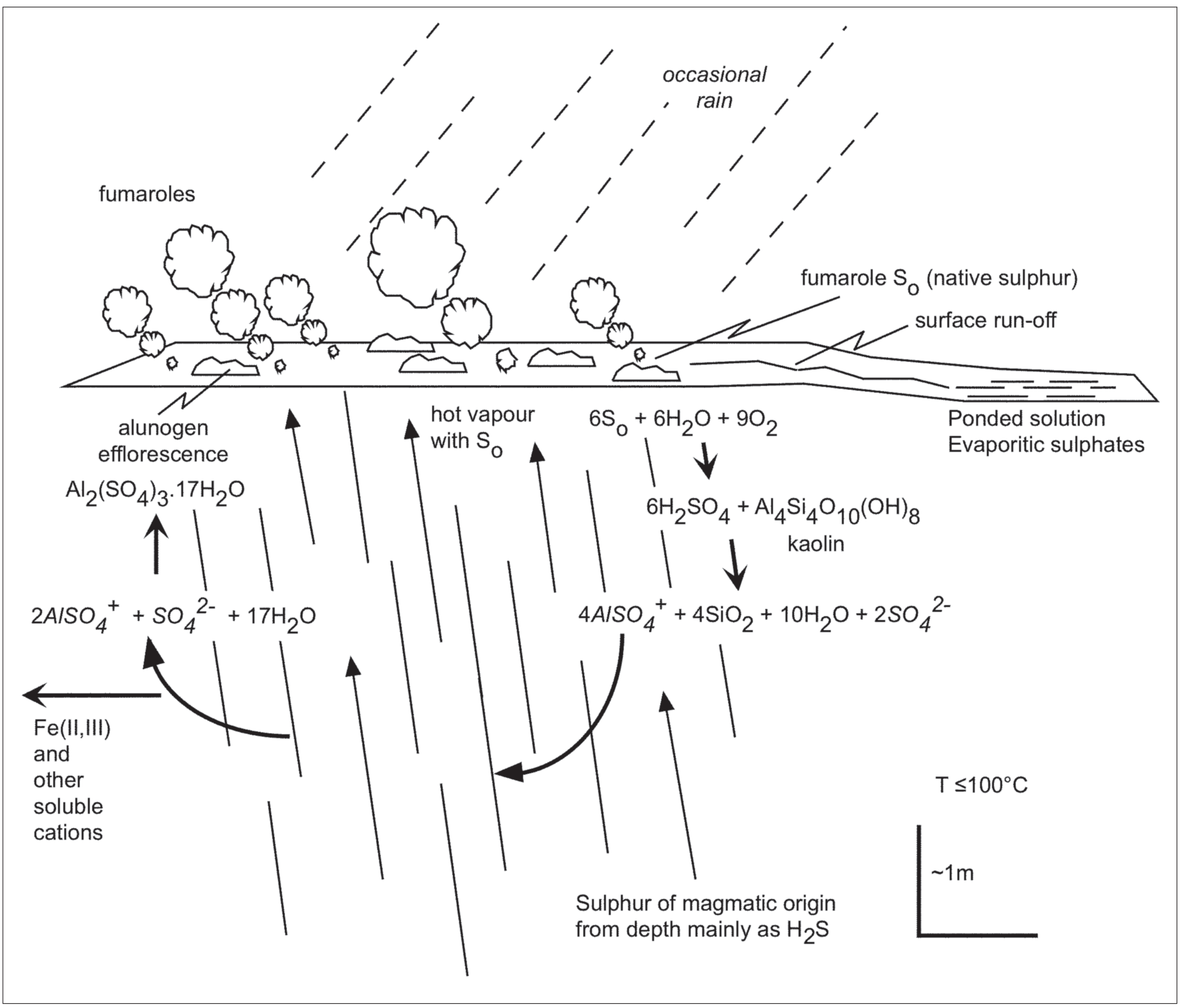
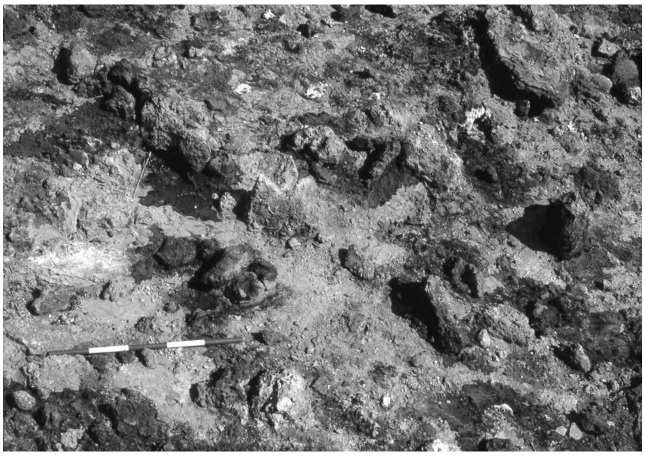


Fig. 6. Model of alum (mainly alunogen production with native sulfur at fumaroles (modified after HALL *et al*., 2003a).



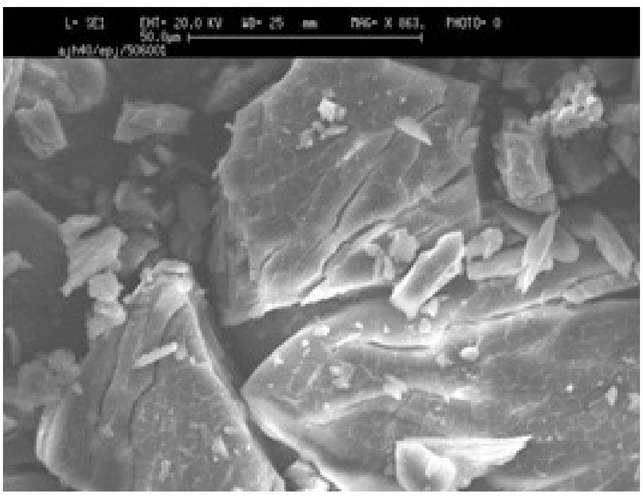


Fig. 7a, Alum at the Aghia Kyriaki solfatara zone. This illustrates how alum appears around sulphurous fumaroles. It would be difficult to harvest large amounts of pure alum as altered tuffaceous material and sulphur would inevitably be included.
Fig. 7b, Platy alunogen, $Al_2(SO_4)_3.17(H_2O)$ viewed in the scanning electron microscope.
Scale bar is 50 microns.

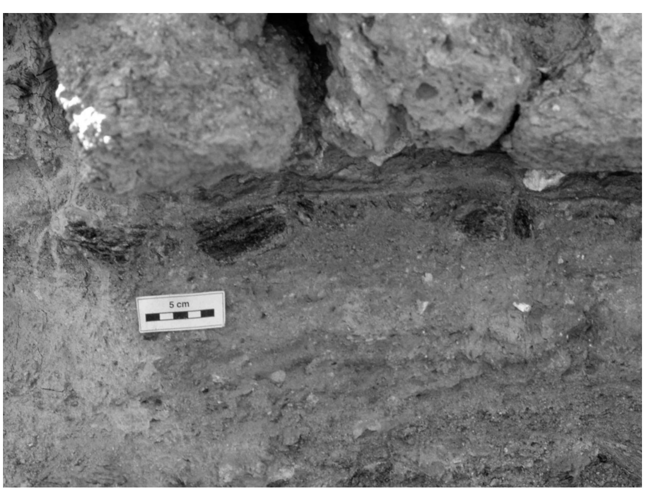


Fig. 8. Reddening in 'veins' of greenish grey sediments close to buried wall at Aghia Kyriaki and now exposed by natural erosion. The reddening has taken place after construction of the wall.

"The entrance is through a narrow passage which leads to certain chambers or hollow places formerly made so, when they wrought for alum. These vaults are four or five foot high, nine or ten broad, incrusted almost throughout with alum, which grows in the form of flat stones from nine to fifteen lines thick. A fast as they take these away, there come new ones; and 'tis plain the Spirit of Salt, which penetrated these stones, did as it were make them exfoliate according their respective veins. The solution of this alum natural and unprepared, is acrid and styptic; it ferments and coagulates Oil of Tartar, in like manner as alum purify'd from which it differs in nothing but having a greater quantity of stony matter" (Tournefort, 1741, 175-176).

Although Tournefort gives a vivid description, it requires careful interpretation. Efflorescences are mineral growths that occur as solutions evaporate from a rock surface. The crystals, often acicular, fibrous or 'fluffy', usually appear to protrude out from, and grow on, the rock surface, but crystal growth also occurs beneath the surface. The solutes are transported in solution and precipitate as the solution evaporates and becomes saturated. Sulphates are common as efflorescences on Melos because the sulphurous geothermal activity produces sulphuric acid which dissolves host rocks. Although the acidic solutions permeate through rock at high temperature, efflorescences typically form at low temperature; their occurrence is therefore not necessarily direct evidence of geothermal activity.

On the other hand, sulphurous fumaroles must be closely related to geothermal activity. Tournefort recorded a sulphurous fumarole in a 'cave', which we have not been able to locate "*....on the sea-shore is another Grotto, the bottom whereof is fill'd with Sulphur, which is incessantly burning, so as there's no going into it. All the places near are continually smoking, and sometimes cast out Flames of Fire; there's seen Sulphur perfectly pure, and as it were sublimated, which is incessantly inflamed in certain places: there are others, from whence distils drop by drop a Solution of Alum, much more acrid than that of common Alum; this Solution is of an almost corrosive Stypticity, and ferments briskly with Oil of Tartar"*. (Tournefort, 1741, p. 179)

All rock-cut cavities in SE Melos appear to have the potential to develop efflorescences on their cavern walls. The development of an efflorescence depends on some water flow through the host rock, the type of host rock and the evaporation conditions. As SE Melos has a semi-arid climate, there will usually be migration of solutes to dry cavern walls as evaporation takes place; if the humidity at the point of potential seepage is high, then the solution is likely to drip out of the rock surface, and wet seepages are anticipated. It is perhaps these wet seepages that Tournefort describes in the following passage:

*".....(and) distils (from the cave) drop by drop a Solution of Alum. According to appearance, this should be that sort of alum, which Pliny calls liquid Alum and which he positively assigns to the Isle of Melos: however, this kind of Alum **was not liquid (**our bold), as may be seen in Dioscorides. It seems*

as if the Liquor which flows from this Grotto should be only a Spirit of Salt, which in Solution contains terrene and aluminous Particles" (TOURNEFORT, 1741, p. 179)

Tournefort feels obliged to make himself clear with respect to Dioscorides and the physical state of this particular form of alum group mineral, which brings to mind the distinction we raised earlier regarding 'liquid' and 'moist' (see above). Its milky appearance may have implied alum in colloidal suspension. Indeed we were in a position to generate such alum, which turned out to be alunogen in the course of field experiments (PHOTOS-JONES & HALL, in prep.).

As alum is very soluble, it can be quite elusive at surface fumaroles but is anticipated to have been more readily available and harvestable in a pure form from deposits at underground fumaroles, ie those within 'caves'. So, once it was recognised to be valuable, fumaroles are likely to have been deliberatly 'tapped' underground to provide a more reliable source of alum. Today an active fumarole in a cave/rock-cut cavity can be seen at Fyriplaka (HALL & PHOTOS-JONES, 2005).

HARVESTING MELIAN ALUM

Alum is easy to collect directly from efflorescences that occur close to active sulphurous fumaroles. If a mine/cavern was driven underground to intersect a fumarole as appears to have been the case at Fyriplaka cave (HALL & PHOTOS-JONES, 2005), it would have been possible to produce pure alum, reliably. Underground workings would also have provided alum in solution as fluid saturated in alum dripped out of fractures in rock as described by Tournefort (see above). Fluid saturated in alum would also have seeped out of rocks at surface fumaroles and this would have been mixed with steam condensate and rainwater. Such fluid could have been trapped in ponds, as alluded to by Pliny (see above) and recovered by evaporitic crystallisation. The precipitate is likely to have been rich in aluminium sulphates but the exact mineralogical nature is difficult to estimate because there are many states of hydration of aluminium sulphates. There would also be other salts present that would co-precipitate with the alum. Ponding of alum in solution would be a transitory feature However, a large area of potential ponding can be seen at Kalamos and smaller areas consisting of walling around fumaroles in Western Palaeochori bay may also relate to deliberate ponding (PHOTOS-JONES & HALL, in prep.).

REAGENTS FOR THE ASSESSMENT OF MELIAN ALUM

We know of two reagents which were used; the first, oil of tartar (a saturated solution of potassium carbonate, K_2CO_3) was a field test and identified presence/absence of ammonium with alum; it was used by TOURNEFORT (1743, p. 176); the second, the juice of the pomegranate, was a reagent for iron-impurity and was used to assess purity. It is mentioned by Pliny.

TOURNEFORT (1741) carried with him oil of tartar to provide a convenient chemical test in the way that modern mineral explorers would carry reaction agents for elements of interest. He states: "*The plumous or feathered alum, which is found there likewise, performs the same alterations when they try'd; but neither of them emits any urinous smell when Oil of Tartar is poured thereon; which allows no room to suspect there is any mixture of Salt Ammoniack*" TOURNEFORT (1743, p. 176).

Tournefort may have had in mind ammonium rich alum, now known as the mineral tschermigite. Or he may, possibly from earlier visits in Italy have been aware of the occurrence of sal ammoniac at fumaroles there (see the Amethyst Galleries website [http://www.galleries.com/Minerals/ HALI DES/sal_ammo/ sal_ammo.htm] last accessed 20 October 2010). We do not know if he considered the presence of ammonium to be a good or bad sign. However, his reasoning must have been as follows: if the Melos alum contained or was associated with ammonium then a reaction with potassium carbonate would give off 'the urinous' smell. However neither the plumous nor feathered alum emitted any such smell. Not knowing the *exact* nature of Melian alum he must have assumed that it had the potential to *contain*, rather than *be*, sal ammoniac or ammonium chloride (NH_4Cl). So he concludes there is "*no room to suspect there is any mixture of Salt Ammoniack*".

Pliny's test, oak galls for paraphoron and the juice of the pomegranate for phorimon was probably not a routine field test but rather probably a quality control test (HALL & PHOTOS-JONES, 2009). The major use of alum in Roman times was as a mordant and any iron present would be disadvantageous (HALL & PHOTOS-JONES *op cit*). Pliny describes the use of pomegranate juice to assess iron content and we have confirmed that this test works well , with only ~300 ppm of iron needing to be present in a solution of alunogen to turn it a dark purple colour (HALL & PHOTOS-JONES *op cit*). Pomegranate juice would, in fact be a useful *field* test for the purity of alum, and it is surprising that Tournefort didn't use it.

EXPERIMENTAL CONSIDERATIONS: POSSIBLE PURIFICATION OF MELIAN ALUM USING FRACTIONAL CRYSTALLISATION

As alum and associated salts are very soluble, it would have been difficult 'refining' alum to attain the purity of material harvested by hand. Experiments were undertaken in the field and laboratory to assess whether fractional crystallisation could be used to purify harvested alum. We suggested that the following three stages may have been involved in the commercial production of Melian alum in Roman times: a) harvesting, b) dissolving in water and heating over hot soils in large open vessels which were allowed to dry in the sun having positioned them at an angle; c) test the collected material for purity. This potential process based on experiments and computational geochemistry has been detailed in HALL & PHOTOS-JONES (2009).

THE 'DISAPPEARANCE' OF LIQUID ALUM AND ITS SIGNIFICANCE FOR THE WANING GEOTHERMAL GRADIENT

'Liquid' alum (*stypteria phorime)* as well as solid forms of alum were available and extracted in the past from Melos. We suggest that alum from Melos was natural, as opposed to artificial alum made from alunite, and it was predominantly alunogen.

The reference to 'liquid' alum has been puzzling particularly since there is little further comment regarding practicalities, like for example how it was collected and or processed. Yet it has been noted in both Roman and 18th century sources. Alum as alunogen of the solid or liquid type, is intrinsically associated with the Melos geothermal activity; the scarcity of liquid alum is therefore corroborating evidence adding to that provided by sediments that the geothermal field is cooling. A cooling system would mean that the hot rock / fluid reaction would be at a greater depth. Such a declining geothermal gradient would be difficult to measure at present as measurement would require a timespan of several hundred years. The slow decline that is proposed would not impact on the potential use of geothermal energy on Melos However, more significantly, declining geothermal activity would mean that there is less chance of a future volcanic eruption on Melos.

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