

Jarosite formation in weathered siliceous chalk in Fontevrault abbey, Loire Valley, France

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Abstract

Jarosite, a hydrous potassium iron sulphate mineral, has been found as the product of weathering in a silicic chalk building stone of a 13th century abbey at Fontevrault (Maine-et-Loire, France). Destabilization of pyrite and glauconite dispersed in the calcareous stone results in the formation of jarosite. The alteration process is probably of very local origin, within the zone in the building stone at its surface where oxidation occurs during wetting and drying on a cyclical basis. The problem of the incompatibility of highly acidic solutions needed to stabilise jarosite ($2.5 < \text{pH}$) within the highly porous, calcareous silicate rock is not explained at present.

KEYWORDS: Jarosite, silicic chalk, weathering.

Introduction

JAROSITE, $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$, has been found in a 2 cm thick oxidized zone at the surface of a building stone from a 13th century abbey (Fontevrault, Loire valley, France). The stone, commonly used in the Loire valley, is the tuffeau, a highly porous silicic chalk of Cretaceous age (Turonian). It is known for its instability under surface climatic alteration conditions.

One of the major processes of alteration can be attributed to water movement through the stones as they dry, either by heating or wind evaporation. These solicitations of climatic change can cause a movement of capillary water in the building stones at or near their surface in the space of several hours (Pisarenco *et al.*, 1996). The movement of water to the surface and its subsequent evaporation is considered to be a motor to change in chemical forces in the surface area of the stone. Because the building stone is continually exposed to climatic change, alteration rates should be at a maximum, compared to geologic environments of alteration under weathering processes where a mantle of altered (reacted) material acts as a buffer between unaltered rock and the chemistry of the atmosphere.

This paper demonstrates mineralogical changes in the surface layer of a porous building stone, which engenders the formation of jarosite.

Jarosite is one of the most important members of the large alunite group of isostructural minerals that may be represented by the generalized formula $RA(\text{BO}_4)(\text{OH})_6$, where R is a monovalent or divalent cation, A is ferric iron or aluminium, and B is sulphur, phosphorous, or arsenic (cf. Botinelly, 1976; Scott, 1987). It has been reported from modern and inferred paleo hot springs (Tkachenko & Zotov, 1974; Cunningham *et al.*, 1984), as a low-thermal diagenesis product (Bauer, 1994), more rarely as a primary mineral in hydrothermal ore deposits (Bertzina *et al.*, 1966; Keith *et al.* 1979; John *et al.* 1991; Stoffregen and Rye, 1992) but most commonly it occurs in acidic, sulphate-rich environments developed as a result of pyrite oxidation during weathering (Nordstrom, 1977). Jarosite precipitation is an important hydrometallurgical technique for removing iron from acidic, sulphate rich solutions at elevated temperatures (Dutrizac, 1980).

In surface environments jarosite is most often found in soil zones. These are the surface portions of the soil profile, those above the water table. This situation is similar to that of the surface layer of the tuffeau building stone in that wetting and drying are the characteristic changes occurring on a regular basis. The porous soils and the porous tuffeau form, in the unsaturated state, a three-phase zone of water and air in the pores and solids of the rock or soil. In

the saturated zones all pores are filled with water and the system is two-phase.

Experimental methods

Electron microprobe (CAMECA MS-46, Université Paris VI, CAMEBAX, Universität Mainz) were used with a 15 kV accelerating voltage, and 12 nA current. In the analysis mode a $5 \times 5 \mu\text{m}$ scanned spot size was used. In the step-scan mode a defocused $40 \mu\text{m}$ spot size was used with steps of $60 \mu\text{m}$. Scanning electron microscope images were made with a JEOL GSM-6100 apparatus. X-ray diffraction was performed on a INEL position sensitive apparatus.

Situation of the study

The building stone investigated in the 13th century Fontevrault Abbey (near Saumur, Maine-et-Loire, France) is a silicic chalk called tuffeau in the Loire Valley of France. This stone, which is still quarried at several sites, is found as building material over a wide area of the Loire valley and has been extensively studied by Dessandier (1995) for its physical and mineralogical characteristics. The material used in the Fontevrault Abbey reported upon by that author is generally a siliceous chalk with high porosity between 38 and 48%. Macro- and microporosity vary in proportion but are somewhat similar in abundance. Our measurement of macroporosity using a surface area count of an SEM image indicates 24–29%, in altered cooxidized as well as unaltered parts of the sample which is compatible with the Dessandier data (14–25%). Permeability to water flow is highly variable (12–238 mD) according to Dessandier (1995). Our sample gave a measured permeability to water of 24 mD.

The Fontevrault chalk contains 30–50% silica found as opal CT or quartz. Minor glauconite (<5%) and pyrite are present as well as alkali zeolites (Dessandier, 1995). In petrographic thin section one can identify small (10–20 μm diameter) glauconite and pyrite grains dispersed in the matrix. Figure 1 shows the general structure of the sample reported on here as seen in scanning electron microscopy.

The tuffeau building stone of the Loire valley is very soft upon extraction and hardens somewhat on exposure to the atmosphere. It is very white upon extraction and becomes variably, slightly brown or yellow upon exposure to atmospheric conditions in place in a building. The change in colour is variable but characteristic for tuffeau stones, being more pronounced in the area of the Fontevrault Abbey.

The weathering of the tuffeau can be very intense producing serious scaling over periods of less than

100 years. This type of weathering is not the subject of our report here. Our material does not present any of this alteration but appears to have remained intact physically while in the wall of the church. The sample taken for study here came from the south-eastern end of the edifice at about a height of 1–2.5 metres. It was found as a discarded block having been replaced by newer material during a recent renovation of the structure. Our sample shows a pronounced honey colour at its surface, typical of much of the façade of the edifice which has yet not been repaired. The blocks of the building stone are 30–50 cm in size.

A brief mention can be made of the geographic and socio-economic site of the Fontevrault Abbey. It was initially established as a refuge from the active world and hence was never near a city nor even a town of any size. This is still the case. Virtually no industry is present in the area. The site, about 180 km from the Atlantic Ocean, indicates that the predominant meteorological effects are oceanic and not influenced significantly by man-made pollution. Hence we assume that the influx of such gaseous contaminants such as SO_2 are minimal. Rainfall is now normally on the order of 735 mm per year. Summers are hot and sunny, the climate is contrasted and mild.

We then assume that the atmospheric weathering of the block in its place in the church wall has been effected by interaction with a rather pure, natural atmosphere.

Mineral phases observed and chemical variation

The sample was studied according to the honey-coloured, oxidized zone and the white, unoxidized part of the sample. The 2 cm thick outer zone is characterized by reddish-brown bands of variable length and thickness. They are difficult to photograph.

Electron-microprobe analyses showed the presence of jarosite in the oxidized zone, in dispersed areas or on the edges of cavities as circular spots assumed to be spheres in three dimensions. No indication of jarosite is found in the unoxidized rock. Table 1 gives the analyses and formulae of selected samples. Most of the analyses indicated an excess of iron compared to the ideal stoichiometric formula, which is probably due to goethite.

In the selected stoichiometric analyses of Table 1, the sodium content is variable. Solid solutions between the two end-members jarosite and natrojarosite can be observed. Microprobe analysis yielded for analyses 38 a composition very close that of 'ideal' jarosite with a K:Fe: SO_4 ratio of 0.92:3.02:1.96 compared to the 1:3:2 ratio.

A multielement linear scan by electron microprobe showed that there is no discernible difference in the

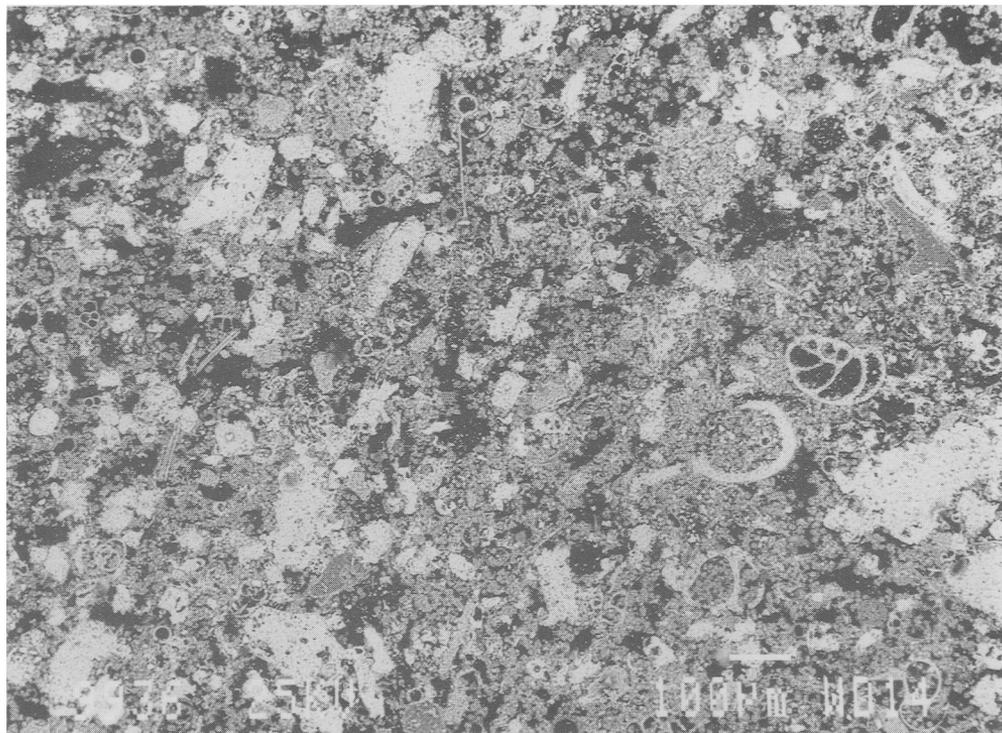
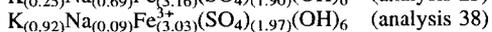
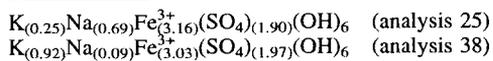


FIG. 1. SEM image of the Fontevrault Abbey stone. White areas are carbonates, grey areas silicates and black areas porosity. Width of the photograph is 1.9 mm.

TABLE 1. Microprobe analyses of jarosite and calculated mineral formula based on six cations, all iron is assumed to be Fe^{2+}

Analysis no. wt. %	23	25	36	38	39	40
SiO_2	0.61	0.22	0.18	0.21	0.12	0.12
Al_2O_3	0.42	0.15	0.31	0.19	0	0.11
FeO	45.52	45.02	45.26	43.92	41.36	42.9
Na_2O	2.01	4.21	2.8	0.54	0.1	0.01
K_2O	6.2	2.36	6.21	8.7	9.24	9.21
SO_3	31.99	30.15	31.3	31.8	31.11	31.94
MgO	0	0.12	0.11	0.23	0.1	0
CaO	0	0	0	0.21	0	0
TiO_2	0	0	0	0	0	0
P_2O_5	0	0.42	0	0.6	0	0
Total	86.75	82.65	86.17	86.4	82.03	84.29



major elements nor in minor elements such as S and Cl between the two zones. Hence we assume that the processes of interaction of the rock with the atmosphere were carried out in an essentially isochemical system, at least on the submillimetric scale. No convection displacement of materials can be evoked. Glauconites in the oxidized zone are frequently brown in colour indicating destabilization.

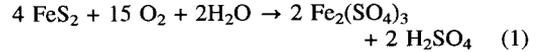
To prove the occurrence of jarosite we prepared a slide with hand picked material from the reddish-brown bands and measured the slide for 3 hours on a INEL position sensitive apparatus. Figure 2 shows the XRD diagram. Jarosite occurs with mica as a minor component. Quartz and calcite are the major phases. No iron oxides were found in this run. With help of the position of the jarosite peaks in Fig. 2 and the *hkl* index from JCPDF file card no. 22-827 we calculated the unit cell dimensions of jarosite (Table 2). Therefore we used the program from Lestinne *et al.* (1990).

Physical changes

No difference in macro-porosity was observed, using SEM methods, in the altered (honey-coloured and banded portion) and unaltered sample.

Origin of the jarosite

Jarosite is common in weathering environments, where it forms in part as a result of pyrite oxidation. The oxidation forms Fe(III)-sulphate which can hydrolyse to goethite and sulphuric acid (equations 1 and 2):



and then



A second, major component of jarosite is potassium. In the tuffeau sample the source would

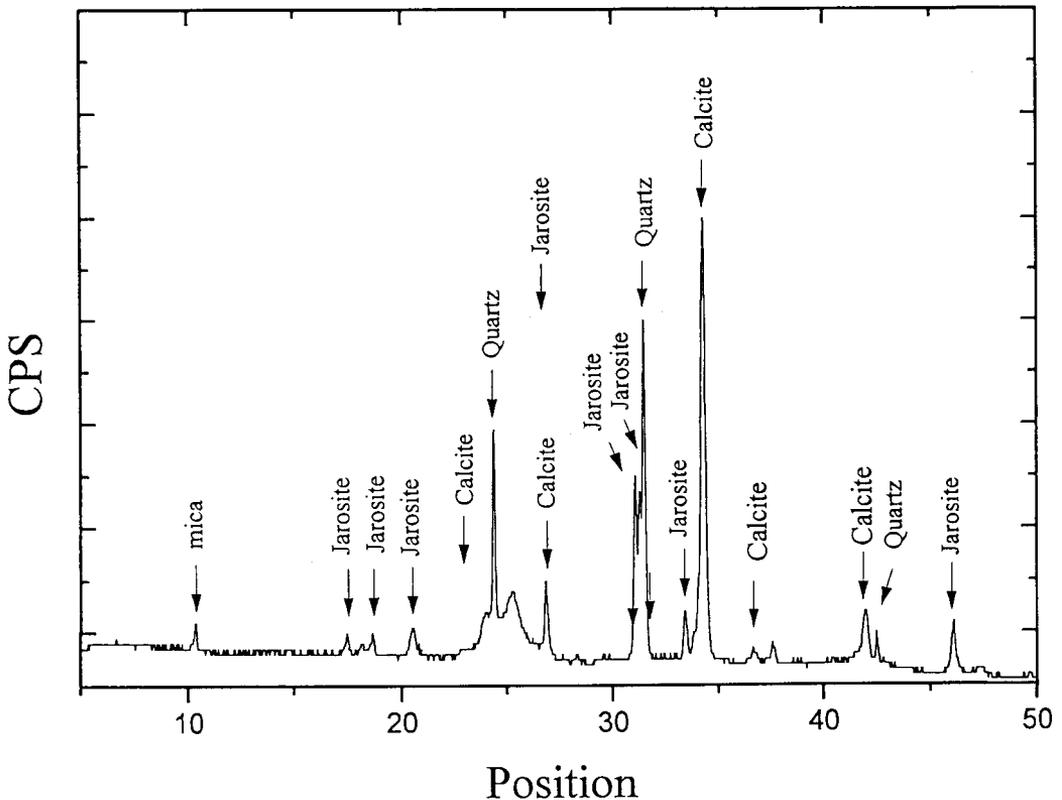


FIG. 2. XRD diagram of material from the reddish-brown bands. Jarosite and mica are minor components beneath quartz and calcite.

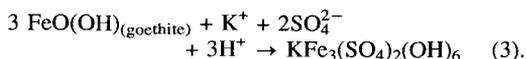
TABLE 2. Comparison of the reported and our calculated unit cell dimensions

System: hexagonal	JCPDF Card 22-827	Calculated values after Fig. 2
<i>a</i>	7.29	7.31 (\pm 0.015)
<i>c</i>	17.16	17.10 (\pm 0.023)

be glauconite. The glauconite and dispersed, very fine grained pyrite are the obvious sources of the major components of jarosite. The presence of jarosite in the oxidized zone of the building stone indicates the destabilization of iron sulphide to form a potassic ferric sulphate mineral.

The stability limits of jarosite are strongly dependent on pH. With increasing pH the jarosite tends to be converted into goethite. Stoffregen (1993) calculated the stability boundaries of jarosite at 25°C based on the thermodynamic data of Alpers *et al.* (1989). Looking at their data it is clear that jarosite can be used as an indicator of acidic, highly oxidising environments. At 25°C the jarosite field extends up to pH 2.17.

If the sulphuric acid is not neutralized the pH decreases. Under these conditions the formation of jarosite from Fe(III) oxides, potassium and sulphur acid occurs by the reaction:



Jarosite in the Fontevrault tuffeau

The building stone in the Fontevrault Abbey has been subjected to wetting and drying cycles for some 800 years on its south-east facing wall. As the stone is little altered physically (porosity) and there is no discernible difference in the distribution of the elements between altered and unaltered zone, one can deduce that the origin of jarosite is due to very local changes in chemistry and migration of elements. No concentrations are observed on the scales of several tens of micrometres, either at the altered-unaltered rock interface or at the outer edge where the stone was in contact with the atmosphere. There is nothing to suggest the transport from outside the rock of elements which could effect the transformations necessary to form jarosite.

Even though the sample was taken at only 2.5 m height in the Abbey wall, splash or surface capillary transport seem unlikely given the overall homogeneity of the elemental composition shown by the electron microprobe scan over altered and unaltered

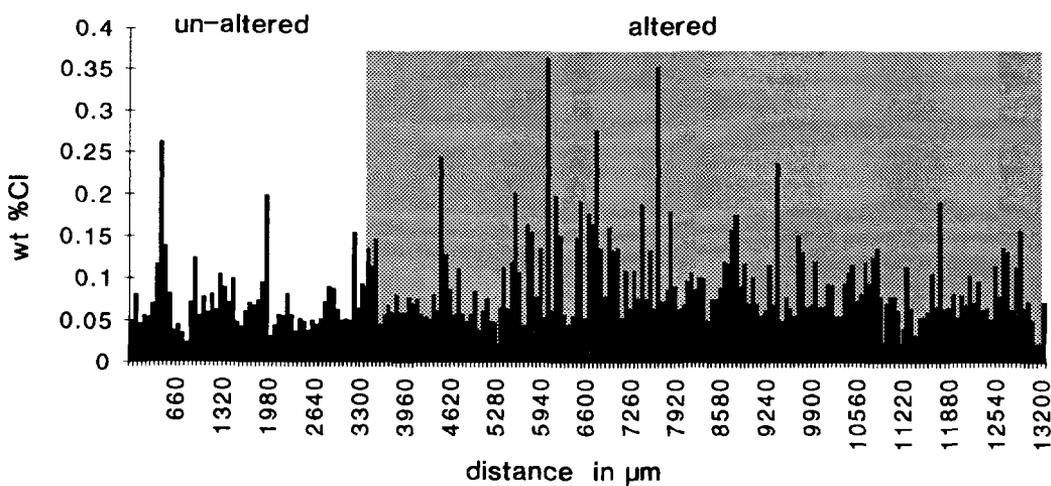


Fig. 3. Traverse of the sample from unaltered area to altered area (greyed zone). Chlorine content is shown in atom weight percent.

zones (Fig. 3). Thus, the oxidation of glauconite and pyrite whose different components combine, very locally, to form jarosite is the process we assume to be at the origin of this mineral.

In the siliceous chalk (tuffeau) the high porosity and probably also high permeability should play a role in the interaction of the rock minerals with atmospheric components. Given lack of evidence for high sulphur content (crusts at the outer edge of the altered zone) we assume that there is a minimal influx of sulphur from the atmosphere. This is reasonable in that the Fontevrault area is unlikely to have experienced sulphur contamination by human activity unlike other areas where rock alteration by scaling is important (Dessandier, 1995). We have essentially a wetting and drying interaction between rock, rainwater and air.

The physical situation, air and water in a porous rock can be compared to another occurrence of jarosite, that of soil profiles. In jarosite-bearing soils, the portion of the system that is continually water saturated is a reducing environment where FeS is stable (De Kimpe and Miles, 1992; Shamshuddin and Auxtero, 1991). However, in soil zones where the water table fluctuates seasonally, oxidation is the rule and iron silicates tend either to be destabilized or change to Fe³⁺ forms (Ducloux *et al.*, 1976). This is true for sulphide-rich soil material, where jarosite is formed. Jarosite is destabilized in its turn when pH is increased, forming goethite (Shamshuddin and Auxtero, 1991; Stahl *et al.*, 1993).

Coming back to the silicic chalk building stone at Fontevrault, the exterior face of the porous stone is subject to fluctuations of drying where oxidation can occur as it does in soils. Also, the excess of iron in jarosite-rich zones indicates that some goethite is present, the typical product of jarosite transformation at higher pH. However, we cannot explain the formation and persistence of jarosite in the same rock which is still predominantly calcite, which should buffer the pH well below the 2.7 value needed for the formation of jarosite.

References

- Alpers, C.N., Nordstrom, D.K. and Ball, J. W. (1989) Solubility of jarosite solid solutions precipitated from acid mine waters, Iron Mountain, California, USA. *Sci. Geol. Bull.*, **42**, 281–98.
- Bauer, A. (1994) Diagenese des Buntsandstein im Bereich der Rheingraben-Weststrandstörung bei Bad Dürkheim. *Mitt. Pollichia*, **81**, 215–88.
- Berzina, A.P., Kuzentsova, I.A. and Sotnikov, V.I. (1966) Hypogene jarosite. *Geol. Geofiz.*, **8**, 112–4 (cited in *Chem. Abstr.*, **66**, 5457).
- Botinelly T. (1976) A review of the minerals of the alunite-jarosite, beudantite, and plumbogummite groups. *J. Res. USGS*, **4**, 213–6.
- Cunningham, C.G., Rye, R.O., Steven, T.A. and Mehnert, H.H. (1984) Origins and exploration significance of replacement and vein-type alunite deposits in the Marysvale volcanic field, West Central Utah. *Econ. Geol.*, **79**, 50–71.
- De Kimpe, C.R. and Miles, N. (1992) Formation of some swelling clay minerals by sulphide oxidation in some metamorphic rocks and related soils of Ontario, Canada. *Canad. J. Soil Sci.*, **72**, 263–70.
- Dessandier, D. (1995) *Etude du milieu poreux et des propriétés de transfert des fluides du tuffeau blanc de Touraine. Application à la durabilité des pierres en oeuvre*. Thèse de 3^{ème} cycle, Université de Tours.
- Ducloux, J., Meunier, A. and Velde, B. (1976) Smectite, chlorite, and a regular interlayered chlorite-vermiculite in soils developed on a small serpentinite body, Massif Central, France. *Clay Minerals*, **11**, 121–35.
- Dutrizac, J.E. (1980) The physical chemistry of iron precipitation in the zinc industry. In *Lead-Zinc-Tin '80* (J.M. Cigan *et al.*, eds), pp. 532–64. AIME.
- John, D.A., Nash, J.T., Clark, C.W. and Wulfange, W.H. (1991) Geology, Hydrothermal Alteration, and Mineralization at the Paradise Peak Gold-Silver and Mercury Deposit, Nye County, Nevada. In *Proceedings of the Great Basin Symposium*, 1020–50. Geol. Soc. Nevada.
- Keith, W.J., Calk, L. and Ashley, R.P. (1979) Crystals of coexisting alunite and jarosite, Goldfield, Nevada. Shorter contributions to *Mineralogy and Petrology*, C1–C5.
- Lestinne, B., Saux, M. and Vdm, R. (1990) *Calcul d'affinement des paramètres cristallins*. Computer Program.
- Nordstrom, D.K. (1977) *Hydrogeochemical microbiological factors affecting the heavy metal chemistry of an acid mine drainage system*. Ph.D. thesis, Stanford University.
- Pisarenco, D., Morat, P. and Le Mouel, J.L. (1996) On a possible mechanism of sandstone alteration: evidence from electrical potential measurements. *C. R. Acad. Sci., Paris*, **322**, 17–24.
- Scott, K.M. (1987) Solid solution in, and classification of, gossan-derived members of the alunite-jarosite family, northwest Queensland, Australia. *Amer. Mineral.*, **72**, 178–87.
- Shamshuddin, J. and Auxtero, E.A. (1991) Soil solution compositions and mineralogy of some active acid and sulphate soils in Malaysia as affected by laboratory incubation with time. *Soil Sci.*, **152**, 365–76.
- Stahl, R.S., Fanning, D.S. and James, B.R. (1993) Goethite and jarosite precipitation from ferrous sulfate solutions. *Soil Sci. Amer. J.*, **57**, 280–2.
- Stoffregen, R.E. (1993) Stability relations of jarosite and natrojarosite at 150–250°C. *Geochim. Cosmochim.*

Acta, **57**, 2417–29.

Stoffregen, R.E. and Rye, R.O. (1992) Jarosite-water ^{18}O and D fractionations. *Amer. Chem. Soc. Div. Geochim.*, **204**, 86 (abstr.).

Tkachenko, R.I. and Zotov, A.V. (1974) Ultra-acid terms of volcanic origin as mineralizing solutions. In

Hydrothermal Mineral Forming Solutions in the Area of Active Volcanism (S.I. Naboko, ed.), 126–31. Oxoniam Press.

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