Deterioration of tuffite and andesite stones monuments in urban areas (Niğde, Central Turkey)

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ABSTRACT

The aim of this work is to investigate the pollution characteristics and the source of pollution on tuffite and andesite walls of 15 historical monuments which were built in various dates in several parts of the Niğde city in central Turkey. In this respect, surface of walls were sampled to represent the general structure of stone monuments. Mineralogical features and structural-textural determinations of rock samples were conducted on thin sections with optical microscopy. The heavy metal accumulations on wall surfaces were measured with Spectro-Xepos Benchtop X-Ray Fluorescence Spectrometer. XRD (x-ray powder diffraction) analyses were also carried out on the same samples. The metal concentrations of the samples were evaluated with coefficient correlation, element coefficient correlation dendogram, hierarchical cluster, model summary and anova analysis statistical methods.

On thin sections, minerals are extensively altered. Chloritization, sericitization, prophylitization, carbonization and limonitization occur on the rock surfaces. Iron oxide is detected along the fracture and fissures. Green, black, yellow, red and brown color changes are seen on the rock surfaces, depending on structural and textural alterations and deterioration. Gypsum also occurs on rocks in association with contamination.

As a result, it was determined that different types of pollutants are involved in pollution of stone monuments. Pollution on the stone monuments has been expedited by

polluted air of the city of Niğde, SO_2 in atmosphere, suspended particular material and exhaust wastes of vehicles. Strong positive correlations were determined among some metallic elements. The elements with positive correlations are thought to have the same source. Determined pollution on tuffite and andesite wall samples from the stone monuments are due to anthropogenic and atmospheric effects. In order to minimize the degree of pollution on stone monuments, necessary measurement should be taken.

Keywords; building material, microenvironment, volcanic rock, heavy metal, geochemistry

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1. INTRODUCTION

In industrial and urban areas, air pollution in association with high metal concentrations causes several environmental problems. Destruction of stone monuments is one of these problems. Varying types of pollutants can expedite the degree of pollution on the stone monuments. Climatic conditions, microbiologic factors, catalyzes, oxidizing metals, organic minerals, clays, high humidity ratio, SO_4^{2-} and NO_x have important effects on deterioration of building stones (Steiger *et* al., 1993; Haynes 1986; Annand and Hudson, 1981; Weber 1985; Vassilakos and Salta 1993; Reddy et al., 1985; Cheng et al., 1987). Deterioration of building stones is expedited with air pollution and particulate material content. SO_2 and SO_4^{2-} are the most important agents for corruption of construction materials. In this respect, black colored sulfate incrusting is one of the most important indicators in determining the degree of pollution on building stones (Cerit, 2002). On rock surfaces, anhydrite ($CaSO_4$) decomposes and facilitates gypsum ($CaSO_4.2H_2O$) formation (Grossi et al., 1994; Moropoulou et al., 1998; Kühnel 2004).

$CaSO_4 + H_2O \rightarrow CaSO_4.2H_2O$ (Grossi et al., 1994; Moropoulou et al., 1998; Kühnel 2004)

In cities with photochemical pollution, NO_x results in alteration of rocks (Sikiotis and Kirkitsos 1994). Environmental problems arising from air pollution is an attractive subject for numerous workers. In association with this kind of pollution, consequences of long-lasting interaction with the stone monuments may cause serious problems. Therefore, the effects of pollution on stone monuments in the Niğde city were investigated with petrographical techniques and geochemical analyses (Moropoulou et al., 1998; Zamudio et al, 2003; Götze and Siedel 2004; Kühnel 2004; Lopez and Garcia 2005; Hosono et al., 2006) as well as Yalcin et al. (2008).

2. Sample origin and extraction

2.1. Regional geology

Considering age, lithology and metamorphism, there are three different tectono-stratigraphic units in the region (Fig. 1). The Tertiary units, Niğde metamorphites, Aladag nappes and Bolkardagı units are uncomformably overlain by the upper Cretaceous-Tertiary rocks (Atabey et al., 1990). These units are overlain by Quaternary volcanic products of the Hasandag- Melendiz Mountains consisting of vitritic tuffite, tufffite breccias and andesite and basaltic volcanic rocks (Copuroglu and Söylemoglu, 2001). In addition to these rocks, kaolinite, opal-CT, illite, smectite, feldspar and alunite are also observed as a result of alteration of volcanic rocks (Copuroglu and Söylemoglu, 2001; Ciflikli and Yalçın, 2001). Tuffite and andesites are the first products derived from the Hasandag- Melendiz volcanism in the study area. The tuffite and andesites used on the walls of stone monuments are supplied from nearby areas.

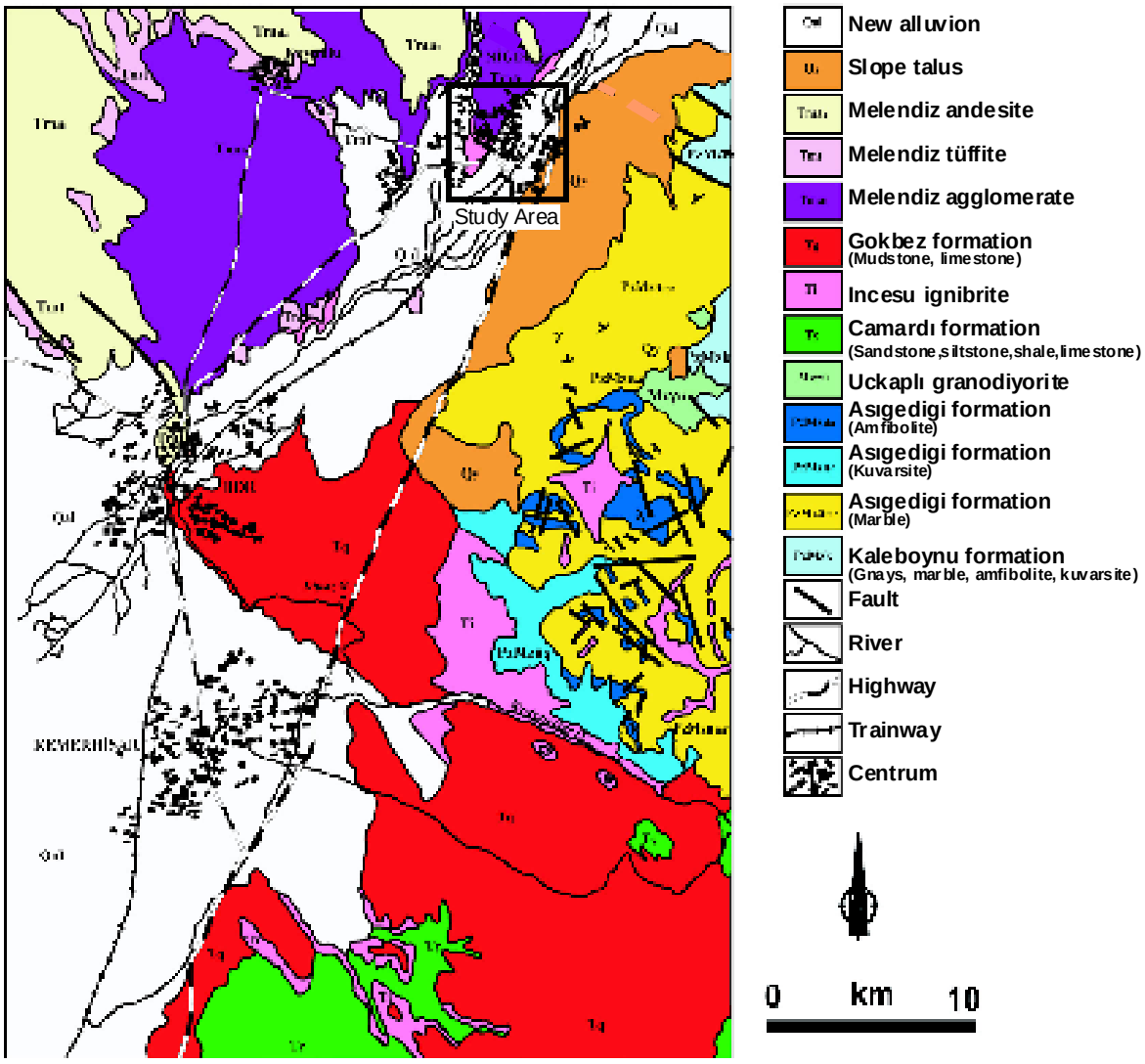


Figure 1. Generalized geological map of the Niğde region (taken from Atabey et al., 1990)

2.2. Study area and monuments

The city of Niğde located in central Anatolia coordinates has a historical importance since the Bronze Era (B.C. 3000-2000) (Fig. 2). It comprises one of the historical settlements in the Cappadocia region. The population of the city is 305,861. Covers are area of 14.294 km^2. Stone monuments under investigation are located in the city center (Güremen et al., 2006). The downtown area has an irregular arrangement. Densely populated parts of the city are very complex (Yalçın and Ulaştı 2000; Yalçın et al., 2005; Yalçın 2007). In periods of intense air pollution, people living in the city are largely affected from the air pollution (Reddy et al., 1985; Cheng et al., 1987).

Monuments with different construction dates are found in varying parts of the city center. In present, most of the stone monuments are used for different purposes. Of these, the oldest one is the Alaattin Mosque and its fountain that were built in the 13th century (Fig. 2).

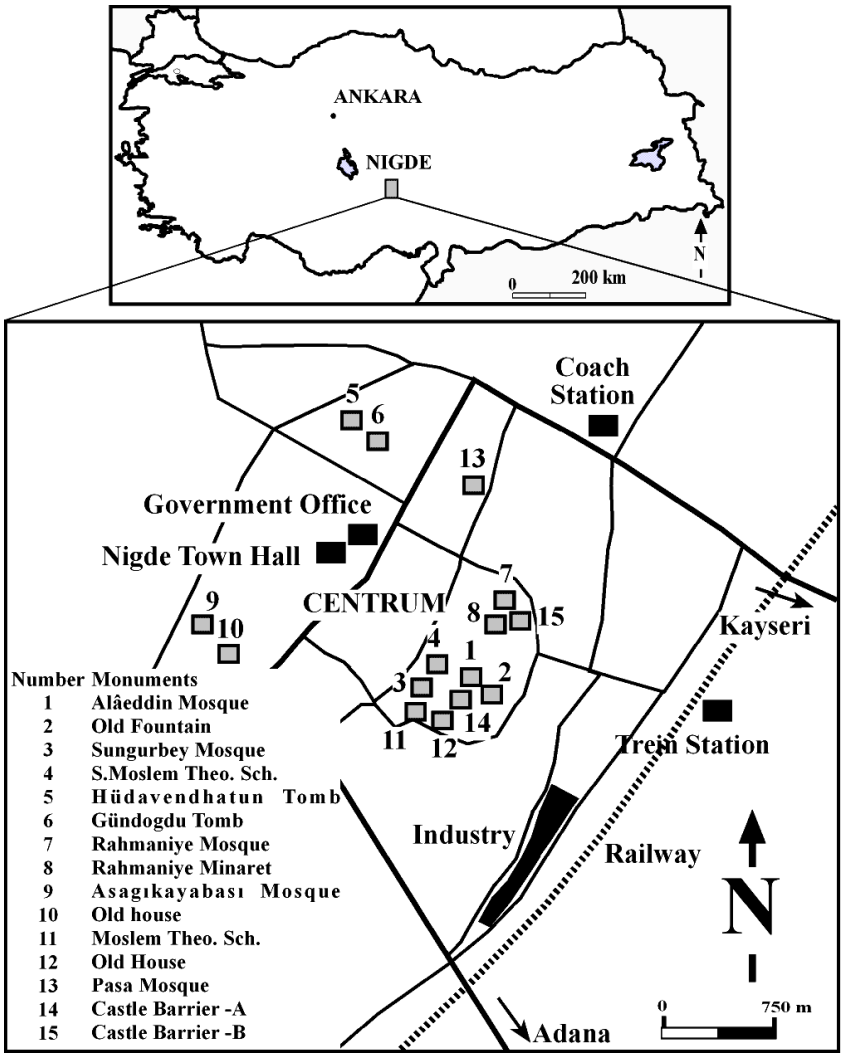


Figure 2. Location and sampling map of the study area

2.3. Atmospheric pollution in Niğde City

Daily average temperatures during the summer (June-August) and winter (December-February) months are 21.13 ^{o}C and 7.57 ^{o}C, respectively. The minimum and maximum temperatures recorded are -27.5 ^{o}C and 38.6 ^{o}C, respectively (Yalçın and Ulaştı 2000; Yalçın et al., 2005).

For the 1998–2004 periods, monthly average concentrations of SO_4^{2-} and suspended particulate material (SPM) exceed the international limit values and yield high values in some cases (Fig. 3). SO_4^{2-} values for 1998, 1999, 2000, 2003 and 2004 years are above 125 μg/m^3, the daily limit value of the World Health Organization (WHO) and the Environment and Climate Program (EU). SPM values for 2003 and 2004 years exceed the EU daily limit value of 125μg/m^3 (Yalçın 2007).

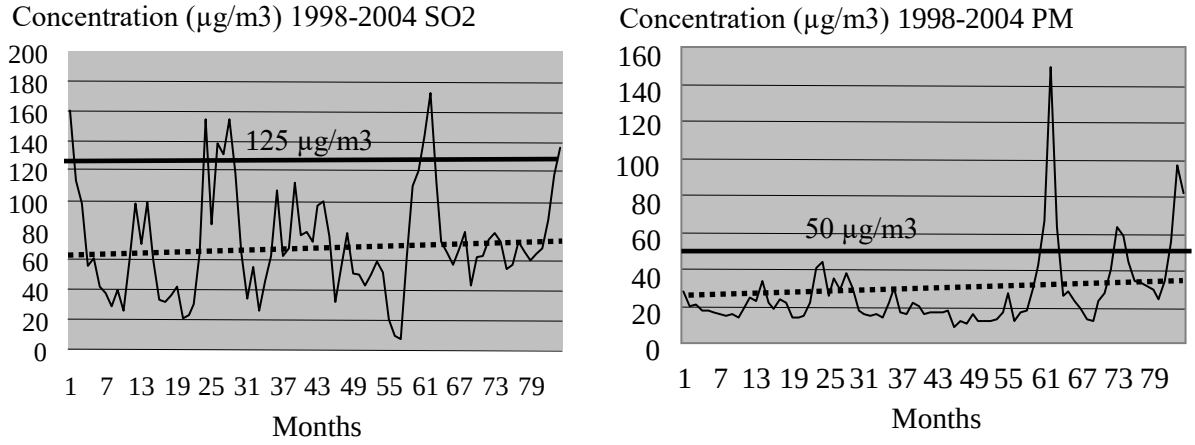


Figure 3. Monthly variations in SO_2 and PM concentrations for 1998-2004 (Yalçın, 2007)

There are about 30 factories in the region and the number of registered vehicles is 4,000. They are; 1 cement plant, 9 textile (e.g. thread, carpet, clothing) plants in the organized industrial site, 2 machinery industry plants, 1 machinery spare part manufacturer, 7 food production facilities (e.g. flour, feed, soft drink), 4 building structure plants (e.g. glass, building structure materials), 4 furniture plants, 1 sugar plant, 1 feed plant, 1 energy power plant and other small-scale plants and facilities (Yalçın et al., 2005). The average traffic load along the stone monuments is 8 vehicles/1 min. In the city center, noise levels associated with traffic load were found as above the limit values (Guremen et al., 2006). In addition, the increasing number of motor vehicles, the use of low-quality fuels as well as heavy winter conditions and the operation of unlicensed heat boilers are the other reasons for the air

pollution to occur in the region. Sulfur and PM concentrations arising from air pollutants are reported to result in serious health problems (Klessis et al., 2000).

The source of pollution in air is stated as high-sulfur oil fuels, liquid fuels and their wastes used in plants and city center. Depending on general increase in SO_4^{2-} and SPM values, air pollution may also cause long-term health problems (Yalçın 2007) and deterioration of stone monuments.

2.4. Sample extraction

Totally 15 samples were collected from stone monuments in the study area. Coarse samples of 1-3 cm thickness were taken from unprotected outer parts of the buildings. Two of the samples were collected from the monuments of 13th century, 4 from 14th century, 1 from 17th century, 2 from 18th century and 6 from 19th century buildings (Table 1).

Table 1. Stone monuments in the Niğde city

Samples	Building	Construction	Origin	Composition
S1	Alâeddin Mosque	1223	Tuffite	Pl, bi, amp, Fe-Ti oks, gyp
S2	Old Fountain	1223	Andesite	Pl, amp, bi, Ol, Clp, Fe-Ti oks, gyp
S3	Sungurbey Mosque	1335	Tuffite	Pl, bi, amp, Fe-Ti oks, gyp
S4	Sungurbey Moslem Theological school	1335	Tuffite	Pl, bi, amp, Fe-Ti oks, gyp
S5	Hüdavendhatun Tomb	1312	Tuffite	Pl, bi, amp, Fe-Ti oks, gyp
S6	Gündogdu Tomb	1344	Tuffite	Pl, bi, amp, Fe-Ti oks, gyp
S7	Rahmaniye Mosque	1740	Tuffite	Pl, bi, amp, Fe-Ti oks, gyp
S8	Rahmaniye Minaret	1740	Tuffite	Pl, bi, amp, Fe-Ti oks, gyp
S9	Asagıkayabası Mosque	1841	Tuffite	Pl, bi, amp, Fe-Ti oks, gyp
S10	Old house	1852	Tuffite	Pl, bi, amp, Fe-Ti oks, gyp
S11	Moslem Theological school	1861	Andesite	Pl, amp, bi, Ol, Clp, Fe-Ti oks, gyp
S12	Old House	1862	Tuffite	Pl, bi, amp, Fe-Ti oks, gyp
S13	Pasa (Murat Ali) Mosque	17. yy	Andesite	Pl, amp, bi, Ol, Clp, Fe-Ti oks, gyp
S14	Castle Barrier (A- Sungurbey Mosque Area)	19. yy	Tuffite	Pl, bi, amp, Fe-Ti oks, gyp
S15	Castle Barrier (B- Castle Area)	19. yy	Tuffite	Pl, bi, amp, Fe-Ti oks, gyp

Pl:Plagioclase; bi:biotite; Amp:amphibole; Fe-Ti okside: Fe-Ti okside, gyp: gypsum; Ol: olivin; Clp: Clinopiroksen (KRETZ,1983)

In order not to disturb the original structure of monuments and to cause an artificial pollution (Figure 4), samples were carefully collected with hammering from coarse tuffite and andesites of the restoration wastes. Sample sizes are at least 10x10x10 cm to be sufficient for chemical analysis and petrographic studies. Samples that were collected systematically were stored in 1-kg plastic bags. Coordinates of sample sites were determined with Garmin brand GPS-12CX device and they were marked on the location map.

3. Analytical Methods

In order to determine petrographical properties, thin sections were made from the samples (Humphries 1992). Thin sections were examined with Nikon brand optical microscope to determine textural and structural features of the samples. Following the petrography studies, characteristic samples were photographed with Nikon-Coolpix 995 brand digital camera.

3.1. Petrographical analysis

Thin sections of rocks samples taken from the walls of stone monuments were examined with optical microscope (Humphries 1992). Thin sections were prepared in accordance with altered parts and unpreserved surfaces of samples. In the collection of hand specimens, disturbance of monuments and artificial pollution were avoided.

Nikon polarizing microscope is an ellipse e400 pol, 230 watt, 0.4 amp, 50/60 herz, Japan, 580157 number microscope.

Determination of modal contents of major minerals and their application to the data were made on the basis of Streckeisen diagram (Streckeisen, 1973). Abbreviations of minerals are according to Kretz (1983).



a: Alâeddin Mosque



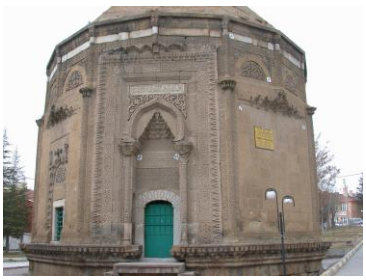
b: Old Fountain



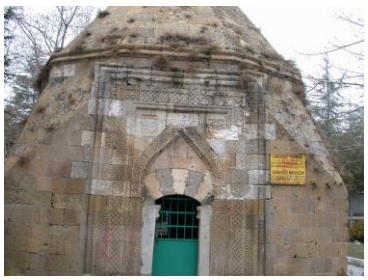
c: Sungurbey Mosque



d: Sungurbey Moslem Theological school



e: Hüdavendhatun Tomb



f: Gündogdu Tomb



g: Rahmaniye Mosque



h: Rahmaniye Minaret



i: Asagıkayabası Mosque



j: Old house



k: Moslem Theological school



l: Old House



m: Pasa (Murat Ali) Mosque



n: Castlebarrier A



o: Castlebarrier B

Figure 4. The studies monuments in the Niğde region (a-o)

3.2. X-ray powder diffraction (XRD)

Before XRD analyses, samples were homogenized with an agate mortar to a grain size of less than 2 mm. The mortar was washed with 6 mol l^{-1} HNO_3 and rinsed with distilled water and dried before the each sample process. Before use, sample bags were washed with 6 mol l^{-1} HNO_3 to avoid from contamination and rinsed with distilled water and then heated at 70ºC.

In addition, in order to determine mineralogical composition of samples, X-ray powder diffraction (XRD, Philips, PW1710 Diffractometer) analyses were also performed. We used 20-30 mg of powder, a support in the form of a Si disk, diffractometer with a rotating sample support. X-ray diffraction was done using a Cu anti-cathode tube at wavelength λ=1.54178Å, scan range 3-75 02θ with 0.02 02θ step size and 10s counting time per step. Diffractograms were evaluated with Mineral Powder Diffraction File Data Book (Bayliss et al., 1980) to identify mineral constituents.

3.3. Geochemical analysis

Chemical analyses were conducted on samples which were homogenized in agate mortar. Analyses of Sb, W, Ag, Mo, Co, V, Cu, As, Sn, Hg, Ni, Zn, Cd, Pb, Si, Al, Fe, Ca, Mg, S, Na, K, Cl, Ti, Cr and Mn elements were performed with X-Ray Fluorescence Spectrometer which name is the Spectro-Xepos Benchtop.

Analyses of homogenized samples were done after they are made double sided film tablets in 32 mm diameter. Detection system is drift detector with Peltier cooling, energy resolution FWHM<170 eV, measured for the Mn-Kα line at 40mA and 40kV with an input count vote of 10.000 pulses, Microprocessor controlled detector and electronics. In these analyses, detection limits ranged from 0.01 to 0.1 wt % for major elements and 0.1 to 5 ppm for trace elements. Results are given as % or ppm.

Metal concentrations of samples were studied with coefficient correlation, element coefficient correlation, dendogram hierarchical cluster, model summary and annova analysis statistical methods with the use of SPSS-11.5 program. Moreover, depending on "element correlations" with SPSS, "element dendogram" were computed with excel program and figures of dendogram were drawn with Freehand 9.0.

RESULTS

Petrographic analysis

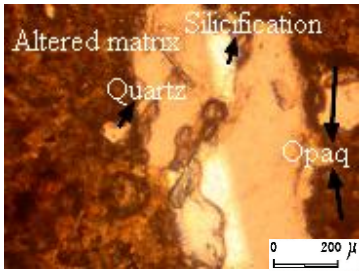
It was found that wall rock of the Alaeddin Mosque is tuffite (Fig. 5a) which hosts an extremely altered matrix and sericitization development. In addition to partly altered pyroxenes, quartz grains are also observed. Wall rock of the stone fountain across the Alaeddin Mosque is composed of andesite (Fig. 5b). Alteration is well developed on outer surface of the rock. However, minerals and matrix within this rock are not altered. Euhedral feldspar crystals are also partly observed. Wall rock of the Sungurbey Mosque is tuffite (Fig. 5c). Extremely altered rock fragments, pyroxene and mesh-shaped olivine minerals were determined.

Wall rock of the Sungurbey Moslem Theological School is also tuffite (Fig. 5d). Extremely argillized feldspar fragments, green colored sericitization/chloritization and yellow carbonization are characteristic. Extremely altered magmatic rock fragments are detected within the matrix. It also contains old volcanic rock fragments (tuffite). Wall rock of the Hüdavend Hatun is also tuffite (Fig. 5e). Extremely altered rock fragments are observed. In addition, red-brown colored iron-oxide and limonitization are also common in fracture and fissures. Wall rock of the Gündogdu is tuffite (Fig. 5f). Yellow colored carbonization is characteristic.

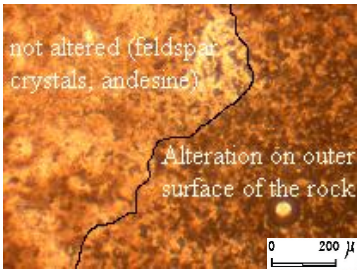
Wall rock of the Rahmaniye Mosque is made up of tuffite (Fig. 5g). Altered rock fragments and microlites are common. Biotite is also partly observed. Wall rock of the Rahmaniye Mosque minaret is tuffite (Fig. 5h). Microlites and feldspars are extremely altered. Rock fragments are partly detected. Wall rock of the Asagıkayabası Mosque is also tuffite (Fig. 5i). Rock fragments are extremely altered. Small quartz grains are characteristic. Opaque minerals are partly observed within the rock fragments. Wall rock of the Historical House is tuffite (Fig. 5j). It is extremely altered. Minerals are peculiar. Pyroxenes are extremely altered. Quartz grains are characteristic in some parts. Serpantinization is also common.

Wall rock of the Moslem Theological School 1861 is andesite (Fig. 5k). Prophylitization was determined in thin sections (Aslaner 1995). Prophylitization is precipitated on the surface of andesite from waters enriched in CO_2 or gas phase (deuteritic). This type of gas-enriched waters also carries some sulfur minerals. Therefore, areas of prophylitization are also enriched in metals. Serpentine (bastite) and calcite (Aslaner 1995) are formed by the alteration of pyroxenes (orthopyroxene). In addition, mesh-textured, eaten olivine is also observed. Matrix is composed of partly altered microlite . Opaque minerals are also observed. In some samples, outer rims of zircon are black colored due to radiation.

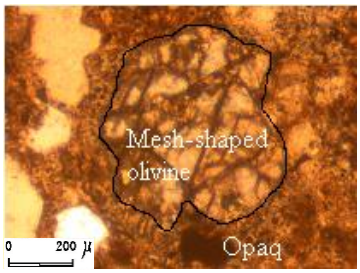
Wall rock of the stone house next to the Moslem Theological School is composed of extremely altered tuffite (Fig. 5l). Quartz is partly observed. Wall rock of the Pasa (Murat Ali) Mosque is made up of andesite (Fig. 5m). It is extremely altered and prophylitization is common which is mostly accompanied by weathered pyrite (Aslaner 1995). Extinction angles of plagioclases are very distinct. The wall rock of castle A is tuffite which hosts an extremely altered matrix (Fig. 5n). Pyroxenes are fractured and sericitization develops along the edges. Biotites are altered. The wall rock of castle B is tuffite with an extremely altered matrix (Fig. 5o). Pyroxenes and biotite are fractured and altered. However, less altered biotites show twinning. Olivine displays mesh-shaped structure.



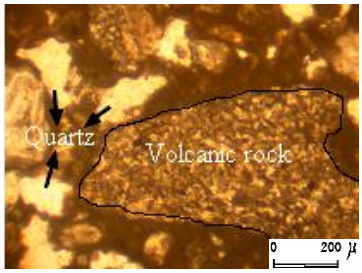
a: Alâeddin Mosque



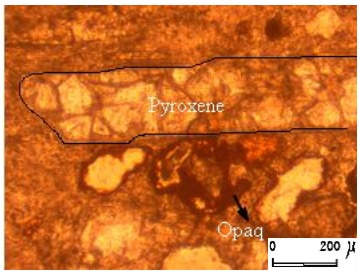
b: Old Fountain



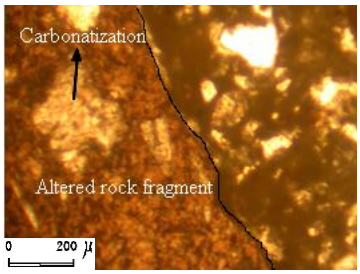
c: Sungurbey Mosque



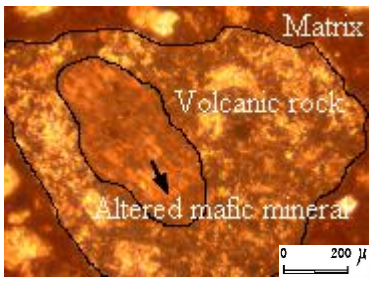
d: Sungurbey Moslem Theological school



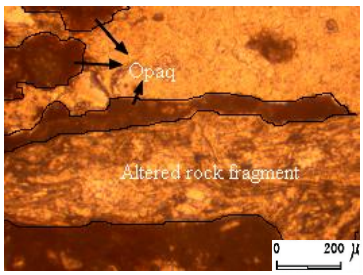
e: Hüdavendhatun Tomb



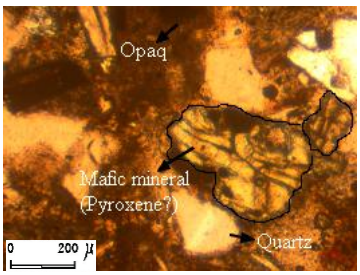
f: Gundogdu Tomb



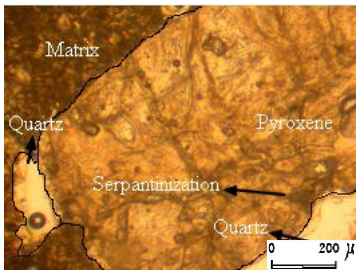
g: Rahmaniye Mosque



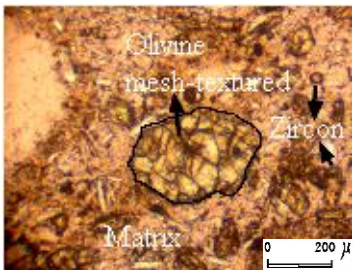
h: Rahmaniye Minaret



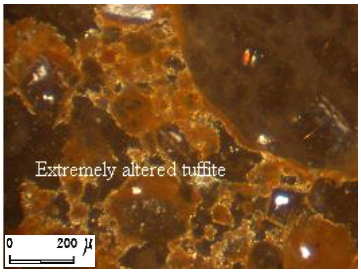
i: Asagıkayabası Mosque



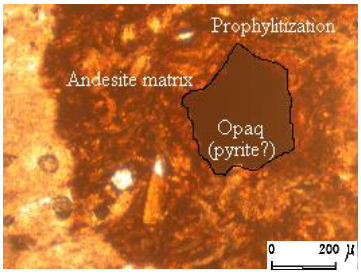
j: Old house



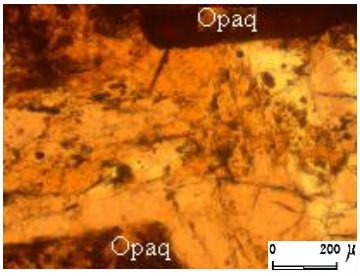
k: Moslem Theological school



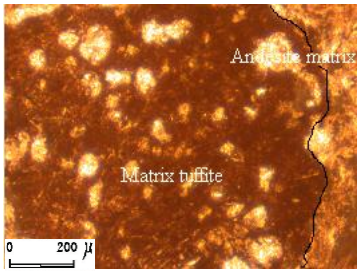
l: Old House



m: Pasa (Murat Ali) Mosque



n: Castlebarrier A



o: Castlebarrier B

Figure 5. Microscopic views of thin sections from stone monuments in the Niğde region (a-o)

X-ray powder diffraction (XRD)

Each sample examined for petrographic studies are used for XRD analysis. Powder samples with grain size less than 0.2 mm were prepared. Results of XRD works revealed the presence of cristobalite, gypsum, halite, muscovite, andesine, jamborite, jarosite, anhydrite, feldspar, sanidin and albite (Fig. 6).

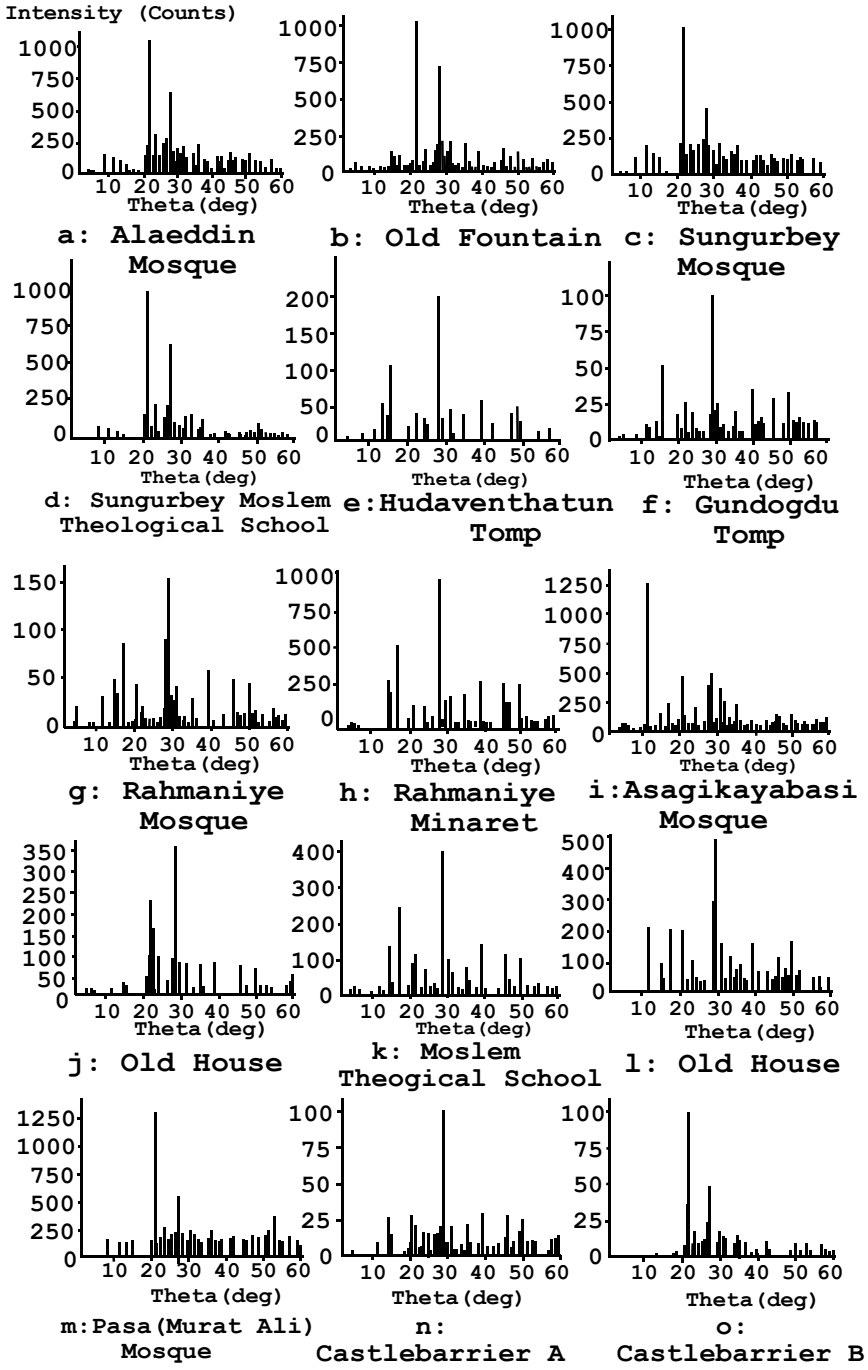


Figure 6. Diffraction patterns of some unsheltered stone samples (a-o)

Geochemical composition

Major and trace elements contents of rock samples collected from walls of stone monuments are given in Table 2.

Results of chemical analyses of tuffite and andesites reported in previous works in the study area and those obtained from the present work were compared. Comparisons indicate that average values of chemical analyses of the present work are higher than those of previous studies. Heavy metals that yielded an anomaly are Cu, Ni, Pb, Al, Fe, Mg, Cl, Ti, Mn, V and Cr (Table 3).

Black incrusting and gypsum formation

Tuffite and andesites used on the walls of stone monuments have been greatly affected from atmospheric pollution. Rock surfaces are washed by the rainwater (1) and then, pyroxene is subjected to prophylitization yielding calcite to occur (2) (Aslaner 1995).

$CO_2 + H_2O$ (rainwater) $\longrightarrow$ H_2CO_3 (1) (Moropoulou 1998)

$H_2CO_3 + CaSiO_3$ (pyroxene: wollastonite) $\longrightarrow$ $Ca(H_2CO_4)\,SiO_2$ (2)

Upon washing of the surface, pyroxene is re-crystallized as larger porous grains (3).

$$Ca(H_2CO_4)\,SiO_2 + H_2O \xrightarrow{\text{Washing}} CaSiO_3 + CO_2 + 2H_2O \quad (3)$$

From surface to the deeper parts of the rock, micro fractures are detected in which salt crystals are developed (Moropoulou 1998) XRD analyses confirmed the presence of halite (Fig. 6). Heavy metal grains are accumulated mechanically in surface of fractures (4). Chemical analyses also confirmed the presence of heavy metals (Table 3). Atmosphere derived heavy metal grains form yellow incrusting on the rock surfaces. Color change was determined in microscopic analyses (Fig. 5). -

Table 2. Chemical composition of samples obtained by XRF (ppm or %)

Coarse	wt % oxides										ppm, trace elements																
Tuffite	SiO_2	Al_20_3	Fe_2O_3	SO_3	CaO	K_2O	Na_2O	MgO	LOI	Total	Ag	As	Cd	Cl	Co	Cr	Cu	Hg	Ni	Mn	Mo	Pb	Sb	Sn	Ti	V	W	Zn
S-1	55	15,45	5,14	1,73	4,48	2,95	2,61	1,53	10,03	98,91	8,4	26,7	4,1	7172	33	312	24,9	1,3	96,6	569	22	23,9	6,1	17,9	3250	109	6	38,1
S-3	55,06	14,35	5,35	0,73	5,49	3,68	2,98	0,74	11,26	99,63	2,9	6,9	4,3	9711	22,1	585	20,2	8	232,7	533	31	20,1	4,8	6,4	1304	18	6,4	32
S-4	55,44	6,97	10,18	6,83	3,70	3,34	1,98	0,76	9,83	99,03	6,9	517,8	3,6	1273	48,1	667	43,3	1,6	266,8	362	60	24,1	6	6,5	3980	181	8,3	28,3
S-5	44,03	5,91	11,05	16,43	6,59	2,66	1,37	0,66	10,53	99,23	3,4	730	4	3241	38	134,6	16	3	56,1	269	22	20,3	5,2	6,4	3478	213	5,9	10,3
S-6	54,25	9,71	8,93	4,33	4,54	4,25	2,84	0,54	10,25	99,64	3,1	34,7	4	12120	20	747	29	1,4	356,8	442	64	20,5	4,8	7,8	1477	20	7,5	32,8
S-7	55,36	5,65	10,85	4,40	5,93	3,93	2,80	0,48	9,86	99,26	2,9	261,6	4,3	11130	32	373	40	2	153,5	312	23	72,3	5,5	6,6	2883	107	6,2	8
S-8	55,47	11,39	5,62	3,48	4,91	3,68	3,25	0,63	10,72	99,13	3,4	72,3	3,8	1964	32,3	924	33,5	1,9	413	558	100	26,2	5,2	6,4	2420	24	8,5	77,9
S-9	52,68	8,87	9,19	6,50	4,49	2,99	2,75	0,30	11,42	99,18	3,8	305,6	4,4	4868	35	625	23,3	3,1	287,4	277	49	23,9	5,4	6,9	3926	213	7,9	19,6
S-10	58,91	8,71	5,59	6,95	3,83	3,89	2,36	0,84	8,05	99,13	7	12,9	4,1	1137	15	288	15	1,5	116	492	21	62	5,8	6,6	1074	17	5,5	21,8
S-12	56,17	16,31	5,98	1,43	1,80	3,33	4,12	0,18	10,04	99,37	4,6	11,3	3,9	269,1	37	596	2437	2,1	213,5	356	56	26,8	5	6,8	3639	26	7,8	50,5
S-14	55,54	7,46	11,72	6,75	1,97	2,58	2,48	0,45	10,31	99,26	4,7	625,1	4,3	2077	53,1	903	66,1	4,4	343,9	268	108	47,3	5	6,5	6117	154	9,1	35,6
S-15	53,65	6,77	11,22	8,00	1,41	3,36	3,28	0,10	11,61	99,40	3,4	462,6	4,3	4899	39	368	32	1,9	157,6	162	28	23,4	5,3	4,3	3653	233	7,5	19,7
MEAN	54,3	9,79	8,40	5,63	4,10	3,39	2,74	0,60	10,32	99,26	4,54	255,63	4,09	4988,43	33,72	543,55	231,69	2,68	224,49	383,33	48,67	32,57	5,34	7,43	3100,08	109,58	7,22	31,22
Coarse Andesite	0																											
S-2	46,35	4,91	15,68	13,35	3,48	3,71	0,31	0,46	10,32	98,58	4,1	761,6	4,4	845,8	70	347	27,4	4,9	154,1	260	28	2,36	5,5	7,7	3803	155	7,7	9,7
S-11	48	5,90	14,69	11,90	3,34	3,48	1,65	0,63	9,06	98,67	4,2	991,9	3,7	2533	99	681	43,4	3,1	269,7	1430	72	24,9	5,7	7,7	4460	349	8,7	24
S-13	44,83	5,78	15,94	12,95	2,16	3,80	1,97	0,30	11,31	99,02	3,5	943,5	4,6	7096	61	306	23	2,5	110	128,6	25	17	5,2	7	2833	375	6,9	12,1
MEAN	46,39	5,53	15,44	12,73	2,99	3,66	1,31	0,46	10,23	98,75	3,93	899,00	4,23	3491,60	76,67	444,67	31,27	3,50	177,93	606,20	41,67	14,75	5,47	7,47	3698,67	293,00	7,77	15,27

Table 3. Variation of concentration values in tuffite and andesite

	Cappadocia Tuffite (Temel ve Göncüoğlu, 1998) A	Tuffite (average) B	Variation of conc. in tuffite (fold) B/A	Cappadocia Andesite (Yurtmen and Rowbotham, 2002)) C	Andesite (avarage) D	Variation of conc. in andesite (fold) D/C
Ag	x	4,54	X	x	3,93	x
Al %	0,41	**5,17**	12,6	0,4 [23-24] 0,52	**2,92**	7,3
As	X	255,63	x	x	899,00	X
Ca %	0,39	**1,17**	3	0,4 [23] 0,5 [24] 0,18	**2,13**	11,8
Cd	x	4,09	x	x	4,23	x
Cl	1126 [21]	**4988,43**	4,43	x	3491,60	x
Co	x	33,72	X	x	76,67	x
Cr	X	543,55	x	9	**444,67**	49,4
Cu	35 [21]	**231,69**	6,6	19	**31,27**	1,6
Fe %	0,29	**5,96**	20,5	0,06 [23] 2,8 [24] 0,17	**10,97**	64,5
Hg	x	2,68	x	x	3,50	x
K %	0,1	**2,8**	28	0,1	**3,03**	30,3
Na %	0,15	**2,01**	13,4	0,08	**0,97**	12,1
Ni	x	224,49	x	18	**177,93**	9,88
Mg %	0,15	**0,36**	2,4	0,06	**0,27**	4,5
Mn	108,9	**383,33**	3,5	38,9	**606,20**	15,58
Mo	x	48,67	X	x	41,67	x
Pb	18 [21]	**32,57**	1,8	34	14,75	-0,43
S %	0,0084 [21]	**2,25**	267,8	x	5,09	x
Sb	x	5,34	X	x	5,47	x
Si %	2,73	**30,01**	10,9	2,8 [23] 2,62 [24]; 2,87	**26,4**	9,1
Sn	x	7,43		x	7,47	x
Ti	785,3	**3100,08**	3,9	261,8	**3698,67**	14,1
V	176 [21]	109,58	(-)0,6	87	**293,00**	3,36
W	x	7,22	X	x	7,77	x
Zn	77 [21]	31,22	(-)0,4	122	15,27	(-)0,13

Conc.: concentration; X: no data; (-): lower conc; %; element datas of revised from table 2

$$Fe, Si, Al, Cu, Ti + O_2 \longrightarrow FeO, FeO_2 \quad (4)$$

In a later stage, previously formed calcite is crystallized from the rainwater. During the calcite formation, anhedral sulfur components are preserved in the environment. Thus, spotted gypsum crystals are developed in areas close to outer parts and, the rock surface transforms to black colored crusting (Fig. 5) (Grossi et al., 1994; Moropoulou 1998).

Results of chemical analyses conducted on soil samples yielded strong correlations for Sb-Ag, W-Mo, Ni-Cr, Ag-Mg, Mo-Ni, Zn-Cr, Co-V, Cu-Fe, V-As, Al-Fe, As-Al-Fe, Sn-Mg, Ni-Cr-Zn and Zn-Al, Cr-Al-Fe and Fe-Ti element pairs. Moderately positive correlations were obtained for W-Co; Ag-Sn; Co-Ti; V-Ti; Cu-Al; As-Ti; Cd-Mn; Al-Mg-Mn pairs. Moderately negative correlations were determined between V and Zn and As and Zn (Table 4). It is thought that metals with high positive correlations have the same source of pollution.

Table 4. Coefficient correlations determined (ppm) for rock samples from walls of the Niğde stone monuments

	Sb	W	Ag	Mo	Co	V	Cu	As	Sn	Hg	Nı	Zn	Cd	Pb	Sı	Al	Fe	Ca	Mg	S	Na	K	Cl	Tı	Cr	Mn
Sb	1																									
W	-,169	1																								
Ag	,766(**)	-,167	1																							
Mo	-,274	,846(**)	-,098	1																						
Co	,226	,534(*)	-,061	,221	1																					
V	,235	,226	-,118	-,102	,755(**)	1																				
Cu	-,252	,132	,030	,099	-,059	-,280	1																			
As	,124	,320	-,196	,025	,852(**)	,892(**)	-,281	1																		
Sn	,489	-,280	,636(*)	-,190	-,024	-,085	-,061	-,224	1																	
Hg	-,438	,055	-,378	-,002	,142	-,036	-,116	,133	-,208	1																
Nı	-,358	,769(**)	-,242	,890(**)	,013	-,264	,007	-,199	-,245	,067	1															
Zn	-,194	,397	,119	,663(**)	-,236	-,523(*)	,344	-,525(*)	,132	-,130	,642(**)	1														
Cd	-,285	-,292	-,319	-,426	-,092	,193	-,217	,133	-,051	,363	-,350	-,492	1													
Pb	,162	-,263	,136	,013	-,336	-,278	-,028	-,290	-,123	-,261	-,043	-,068	,014	1												
Sı	,027	,656(**)	,183	,639(*)	-,045	-,333	,349	-,372	-,143	-,170	,696(**)	,622(*)	-,337	,136	1											
Al	-,128	,088	,360	,337	-,441	-,687(**)	,595(*)	-,764(**)	,348	-,153	,368	,803(**)	-,369	,049	,566(*)	1										
Fe	,199	,413	-,181	,045	,840(**)	,817(**)	-,256	,925(**)	-,171	,123	-,148	-,509	,176	-,274	-,207	-,750(**)	1									
Ca	-,089	-,530(*)	,053	-,245	-,463	-,327	-,305	-,264	,243	,072	-,185	,078	-,174	-,237	-,547(*)	,040	-,405	1								
Mg	,419	-,269	,668(**)	-,064	-,340	-,347	-,190	-,497	,789(**)	-,130	,004	,388	-,245	-,088	,041	,528(*)	-,506	,435	1							
S	,161	,052	-,174	-,169	,522(*)	,608(*)	-,354	,787(**)	-,249	,110	-,356	-,563(*)	,098	-,280	-,489	-,824(**)	,793(**)	,117	-,487	1						
Na	-,293	-,108	,106	,169	-,580(*)	-,805(**)	,547(*)	-,828(**)	,137	-,057	,311	,728(**)	-,349	,009	,381	,890(**)	-,874(**)	,266	,401	-,769(**)	1					
K	-,290	,319	-,144	,298	-,088	-,336	,083	-,307	-,158	,071	,550(*)	,441	-,368	-,445	,413	,389	-,360	,130	,141	-,363	,540(*)	1				
Cl	-,293	-,390	-,360	-,296	-,369	-,114	-,317	-,272	,185	,072	-,025	-,219	,358	,122	-,364	-,057	-,296	,211	,210	-,374	,052	,042	1			
Tı	,139	,637(*)	,086	,430	,637(*)	,522(*)	,104	,588(*)	-,009	,038	,134	-,082	-,031	-,083	,221	-,227	,733(**)	-,527(*)	-,306	,439	-,569(*)	-,423	-,459	1		
Cr	-,325	,805(**)	-,147	,931(**)	,079	-,239	,097	-,173	-,189	,102	,976(**)	,681(**)	-,374	-,005	,732(**)	,442	-,130	-,268	,042	-,402	,318	,474	-,093	,238	1	
Mn	,269	,214	,138	,283	,447	,107	-,061	,095	,228	,036	,252	,222	-,574(*)	,001	,146	,134	,011	-,030	,191	-,107	,112	,322	-,087	,005	,290	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).

Hierarchical Cluster Analysis dendogram for the chemical analyses reveals some similarities for some samples. Samples with similarities can be divided into two groups. In this respect, stations with similar features have the same pollution source (Fig. 7).

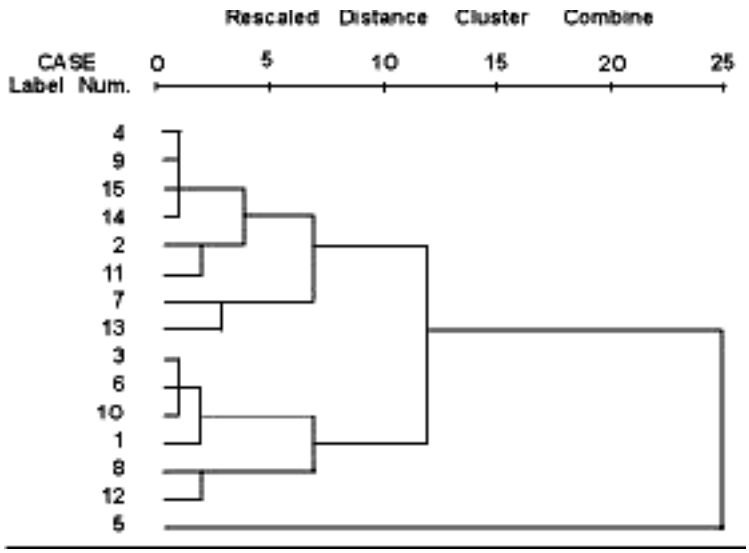


Figure 7. Hierarchical Cluster Analysis dendogram for the samples from stone monuments

In the regression data on Pb concentrations, model summary and anova tables were prepared (Table 5). Coefficient of determination of the regression equation for Mode Summary is R^2= 100 % which yields a significant correctness. On the basis of anova, 14 determinant variables (Mn, Ti, Hg, Cu, Ni, Mg, Cl, Ca, K, V, Cd, Zn, Co, Sb) significantly determine the variation in Pb concentrations.

Table 5. Model summary and anova (b) tables for the regression data

Model summary				
Model	**R**	**R Square**	**Adjusted R Square**	**Std. Error of the Estimate**
1	1,000(a)	1,000	1,000	.
a Predictors: (Constant), Mn, Ti, Hg, Cu, Ni, Mg, Cl, Ca, K, V, Cd, Zn, Co, Sb				

Anova(b)						
Model		**Sum of Squares**	**df**	**Mean Square**	**F**	**Sig.**
1	**Regression**	4516,499	14	322,607	.	.(a)
	Residual	,000	0	.		
	Total	4516,499	14			
a Predictors: (Constant), Mn, Ti, Hg, Cu, Ni, Mg, Cl, Ca, K, V, Cd, Zn, Co, Sb						
b Dependent Variable: Pb						

DISCUSSION

Tuffite and andesite were used on the walls of 15 stone monuments in the city center of Niğde. In thin sections, extremely altered rock fragments, matrix, biotite, plagioclase, clinopyroxene, amphibole, Fe-Ti oxides, mesh-shaped olivine, gypsum and quartz crystals were observed. XRD analyses yield the presence of cristobalite, gypsum, halite, muscovite, andesine, jamborite, jarosite, anhydrite feldspar, sanidine and albite. Gypsum content decreases in samples collected from deeper sections of rocks (Thomson and White 1974; Schuster and Reddy 1994), which is due to the fact that rainwater washes or dissolves rocks towards the bottom. In addition, SO_4^{2-} in air is absorbed on carbonate rocks in association with humidity (Henricsen 1994).

The various material-environment interactions taking place are characterized by: yellow patinas on washed-out areas, firmly attached black-grey crusts in contact with water, black loose deposits and gypsum in rain watersheltered areas and cementitious crusts coating and pitting horizontal surfaces (Moropolu, et al., 1998). It was determined that surface of walls was polluted which resulted in alteration of wall rocks from surface to the inward. Alteration effects in minerals are shown as green colored sericitization, black colored chloritization and yellow colored carbonization. Along the fracture and fissures, red-brown colored iron oxides and limonitization are also distinct. Gypsum that is formed as a result of prophylitization is shown as black incrusting on the rock surface.

Chemical analyses indicate that Cu, Ni, Pb, Al, Fe, Mg, Cl, Ti, Mn, V and Cr have high concentrations. Elements that yield strong positive correlations such as Ni-Cr; V-As, Al-Fe; Ni-Cr-Zn; Al-Fe; Fe-Ti, probably have the same origin. This relation is confirmed by the model anova (Table 5). Coefficient of determination for the model summary for Pb element is

R^2= 100 %. On the basis of anova, 14 determinant variables (Mn, Ti, Hg, Cu, Ni, Mg, Cl, Ca, K, V, Cd, Zn, Co, Sb) significantly determine the variation in Pb variations.

There are two sources of pollution for tuffite and andesites which were used in stone monuments. The first, the most important one, is the polluted air of Niğde city. For the 1998–2004 periods, monthly average concentrations of SO_4^{2-} and suspended particulate material (SPM) exceed the international limit values and yielded high levels in some cases (Yalçın 2007). The polluted air, especially during the winter period, has a negative effect on the surface of stone monuments. This results in alteration of rocks and changes their physical appearance and mineralogical structure (Moropoulou 1998; Riganti et al., 1993; Keppens et al., 1985). The second source of pollution is the heavy traffic in the city. Stone monuments are cramped with new buildings and narrow streets. Therefore, heavy metal anomalies on wall surfaces are most probably related to exhaust wastes of the vehicles. In areas of lesser amount of traffic load and those exposed to open air, heavy metal concentrations are lower (Table 1).

CONCLUSION

It was determined that tuffite (Alâeddin Mosque, Sungurbey Mosque, Sungurbey Moslem Theological school, Hüdavendhatun Tomb, Gündogdu Tomb, Rahmaniye Mosque, Rahmaniye Minaret, Asagıkayabası Mosque, Old house, Old House, Castle Barrier A- Sungurbey Mosque Area, Castle Barrier B- Castle Area) and andesite (Old Fountain, Moslem Theological school and Pasa -Murat Ali- Mosque) samples from stone monuments are polluted and, depending on this pollution, deterioration and alteration (chloritization, sericitization, prophylitization, carbonization and limonitization) are developed on washed-out areas, in contact with water, in rain water-sheltered areas and cementitious crusts coating and pitting the horizontal surfaces. In association with structural and textural alterations, green, black, yellow, red and brown color changes are observed. Gypsum occurs on rocks in

association with contamination. Iron oxide is detected along the fracture and fissures. Anthropogenic and atmospheric agents are the sources of this pollution. In order to minimize the degree of air pollution on stone monuments, necessary measurement should be taken.

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