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# AN APPROACH TO THE ORIGIN OF KEBAN LEAD-ZINC MINERALIZATIONS, ELAZIĞ, TURKEY: A PRELIMINARY STUDY

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ABSTRACT. _ Mineralizations at Keban and its surroundings are generally observed at the contacts of granitoids and epimetamorphic rocks, in Nimri formation and in Keban marbles. Lead-zinc mineralizations in this region are previously interpreted as skarn type occurrences associated with granitoids. In this study, predominantly carbonate mineralizations in the carbonate rocks of Nimri formation and sulphide and carbonate ores within the Keban marbles are investigated. As a result of mineralogical, petrographical and geochemical studies, some significant evidences indicate that the mineralizations are not directly related with the skarn type associated with granitoids. According to the limited data collected during this study, the view that the mineralizations, present in Nimri formation and Keban marble, are mobilized with the influence of granitoids becomes significant. Mineralizations taking place earlier than mobilization are discussed by exhalative sedimentary (SEDEX) type and Mississippi Valley Type (MVT) relying on the present data. Some evidence is found for SEDEX type. While primary occurrences are getting their new positions by means of secondary processes, metallic contents of primary occurrences are enriched. Mobilizations related with metamorphism and/or granitoid impact and enrichment processes caused by weathering are out of the study. The main result of this study is the necessity of new other revitalization of discussions about the origin of primary occurrences for contribution to science and economy.

## INTRODUCTION

The Keban region has been subjected to a number of investigations and studies of many geologists because of copper-molybdenum-fluorite-tungsten-vanadium ores known since the 18. century and engineering problems with Keban dam located at the north of Keban town.

Lithologies in the studied area have been investigated and the regional stratigraphy is attempted to be constructed by various geologists at different times. The approaches by those geologists for lithostratigraphic sequence are correlatively illustrated in Figure 1. Studies about the basement are represented by Özgül, 1981 and Özgül and Turşucu, 1984.

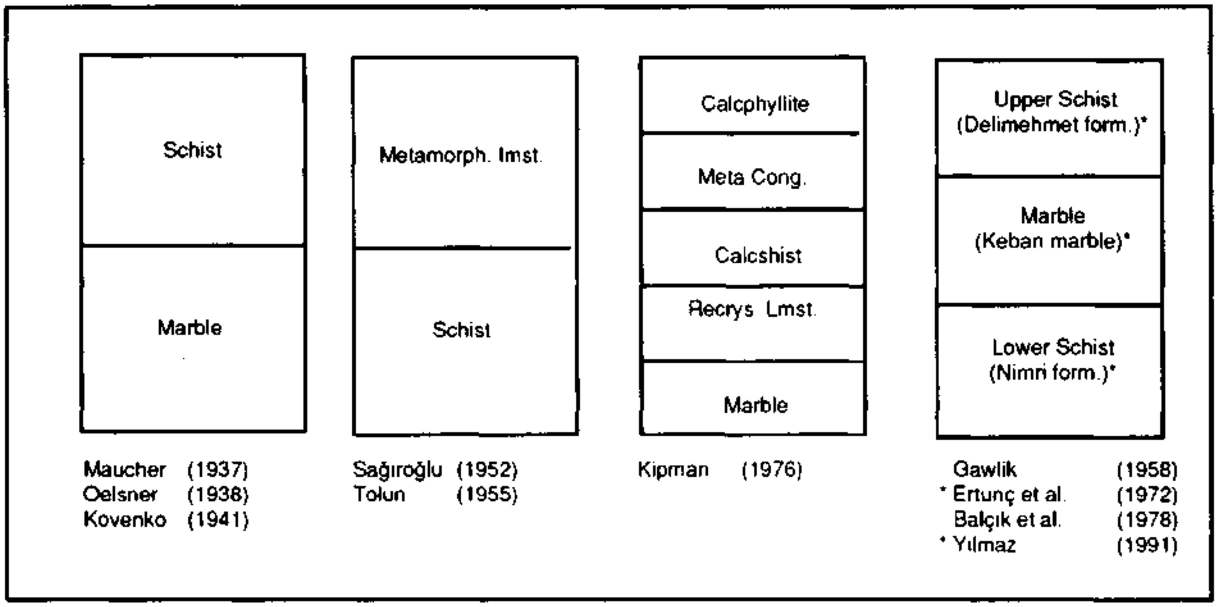

Fig. 1 - Lithostratigraphic sequences around Keban schematized according to various authors.

The major mining geological studies made in this region are as follows: Fishbach, 1900; Ami, 1937; Maucher, 1937; Kovenko, 1941; Kumbasar, 1964; Ziserman, 1969; Kineş, 1971; Köksoy, 1972; Balçık et al., 1978; Balçık, 1979; İTÜ, 1981; Yılmaz et al., 1983; Çağlayan, 1984; Öztunalı, 1985-1989.

Main technological studies are: Canbazoğlu, 1986; Demirocak et al., 1986 and Göktekin and Önal, 1986.

Two different views about the ore formation are introduced with previous mining geological studies. The first view about mineralization suggests that the origin of ore elements are related with granitic rocks based on the position of mineralizations at the contact between syenite porphyry and Keban marble and/or schists, which tend to develop into the Keban marbles. Meanwhile, accompaniment of pirometasomatic, pneumatolitic, hydrothermal stages and skarn minerals with the mineralizations form additional evidence for contact type occurrences (Fig. 2). In contrast, the second view puts forward the view that the mineralization must have originated from host rock and granitoidic intrusions into the above mentioned units and played an effective role for today's position of mineralizations mobilizing the low metal concentrations from the units (Fig. 3).-

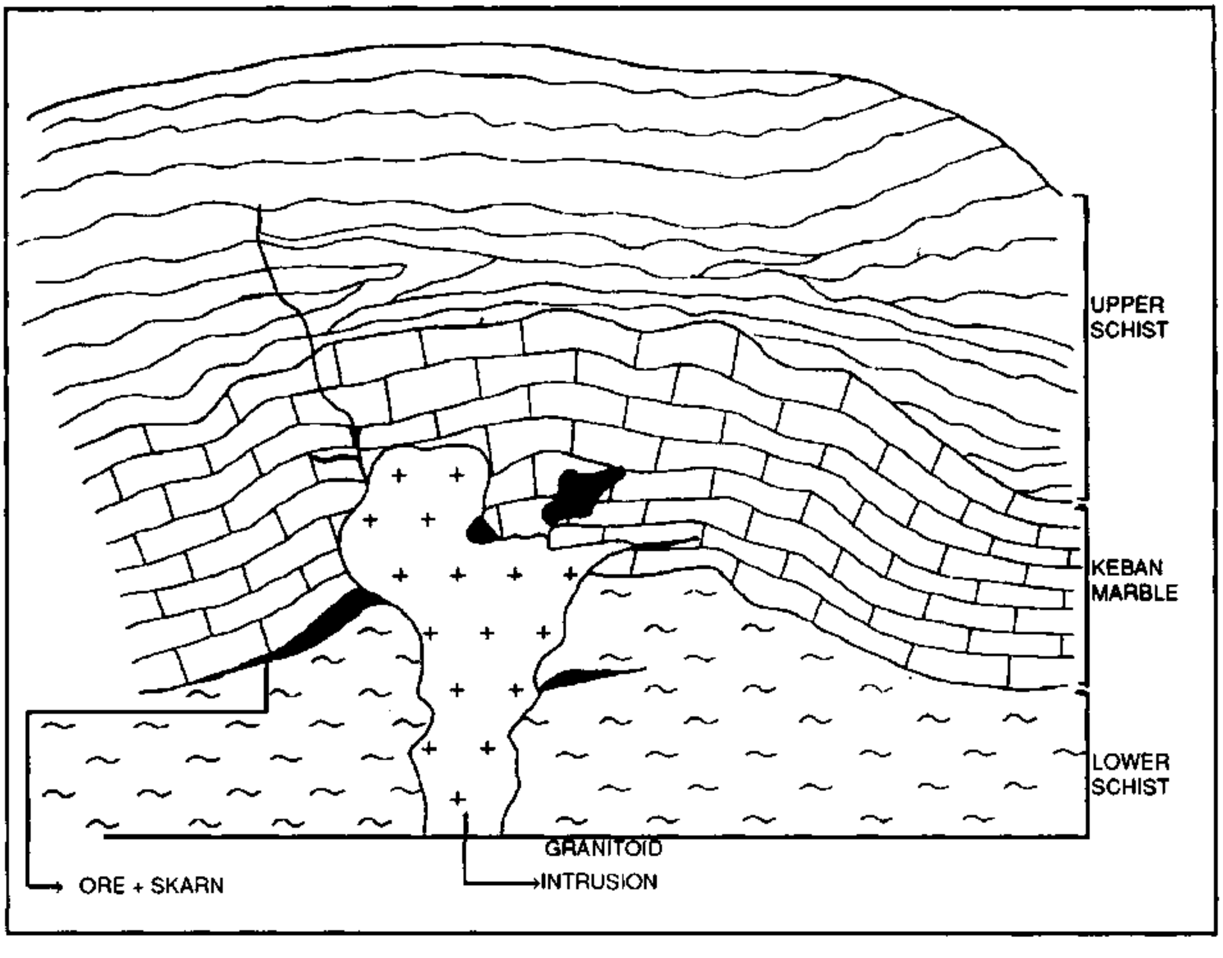

Fig. 2 - Ore forming model directly related with granitoids (schematized after Arni 1937, Köksoy, 1972 and Çağlayan, 1984).

In previous studies, mining geological data pectuar to ore occurrences described as skarn type are discussed in detail. In this study, primary occurrences, belonging to the pre-stage described as skarn, are investigated by means of mineralogical, petrographical, geochemical, and geostatistical methods and the findings obtained are discovered.

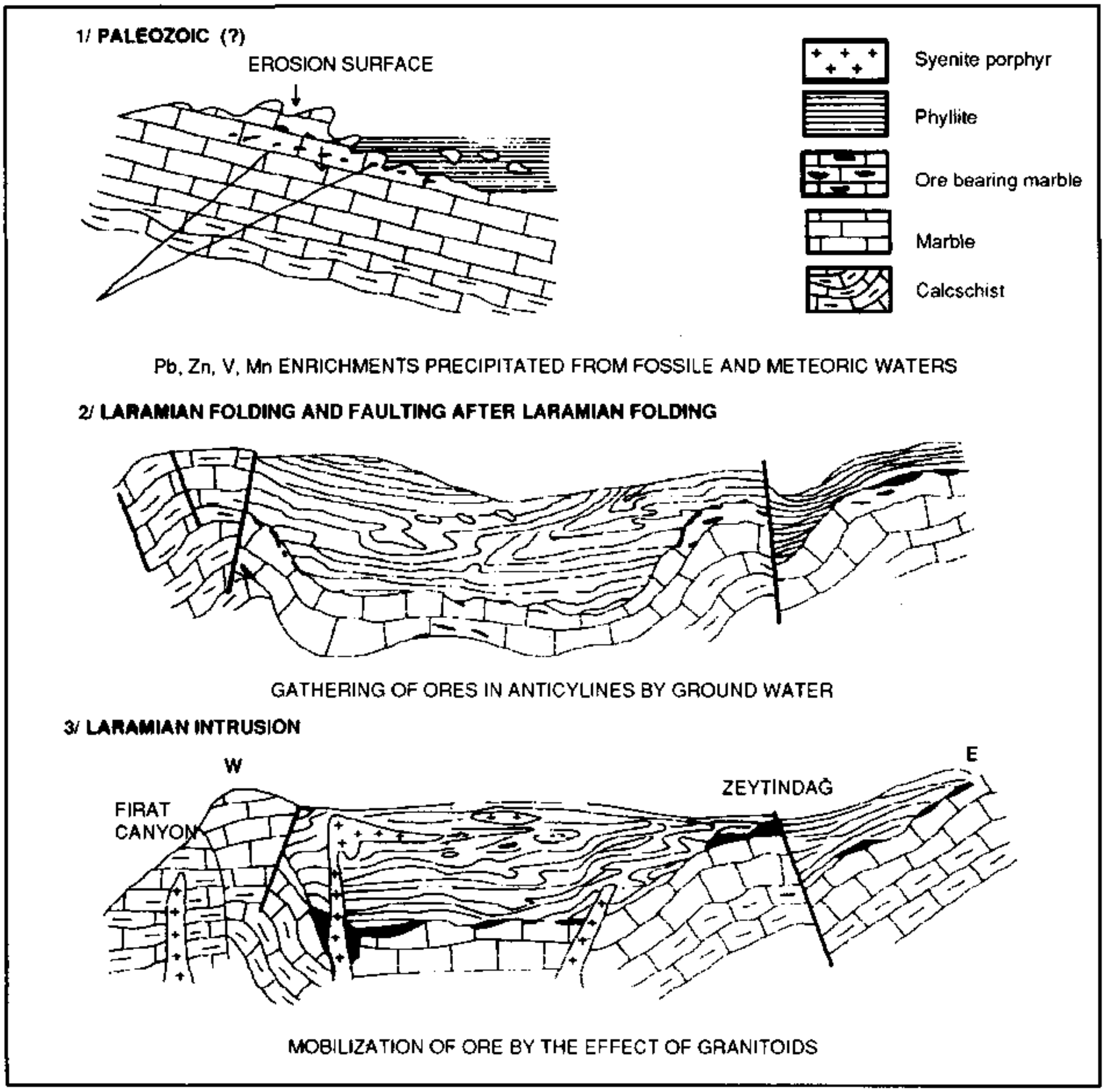

Fig. 3- Ore forming model indicating that the mineralizations in country rocks are mobilized by granitoid intrusions (after Ziserman, 1969).

## GEOLOGICAL SETTING, FIELD RELATIONS AND PETROGRAPHY

The Keban area is located at the Eastern Taurus region of Tauride tectonic belt which is one of the tectonic units of Anatolia. The stratigraphic sequence of the studied area can be summarized from older to younger as Nimri formation, Keban marbles and Delimehmet formation. Low angle unconformities are seen between these units (Fig. 4 and 5). These Paleozoic (Permocarbonifer) aged units are influenced by low grade metamorphism (epimetamorphism) and are intruded by syenite porphyries which are the products of magmatic activity that occurred at the beginning of the upper Cretaceous or Eocene (Ertunç et al., 1972; Yılmaz, 1991).

At the bottom of Nimri formation crops out gray colored, porous Arapkir limestones which are made of fine grained, equgranular calcites and accessoric xenomorph quartz. This unit is overlained by calcschists, a domi-

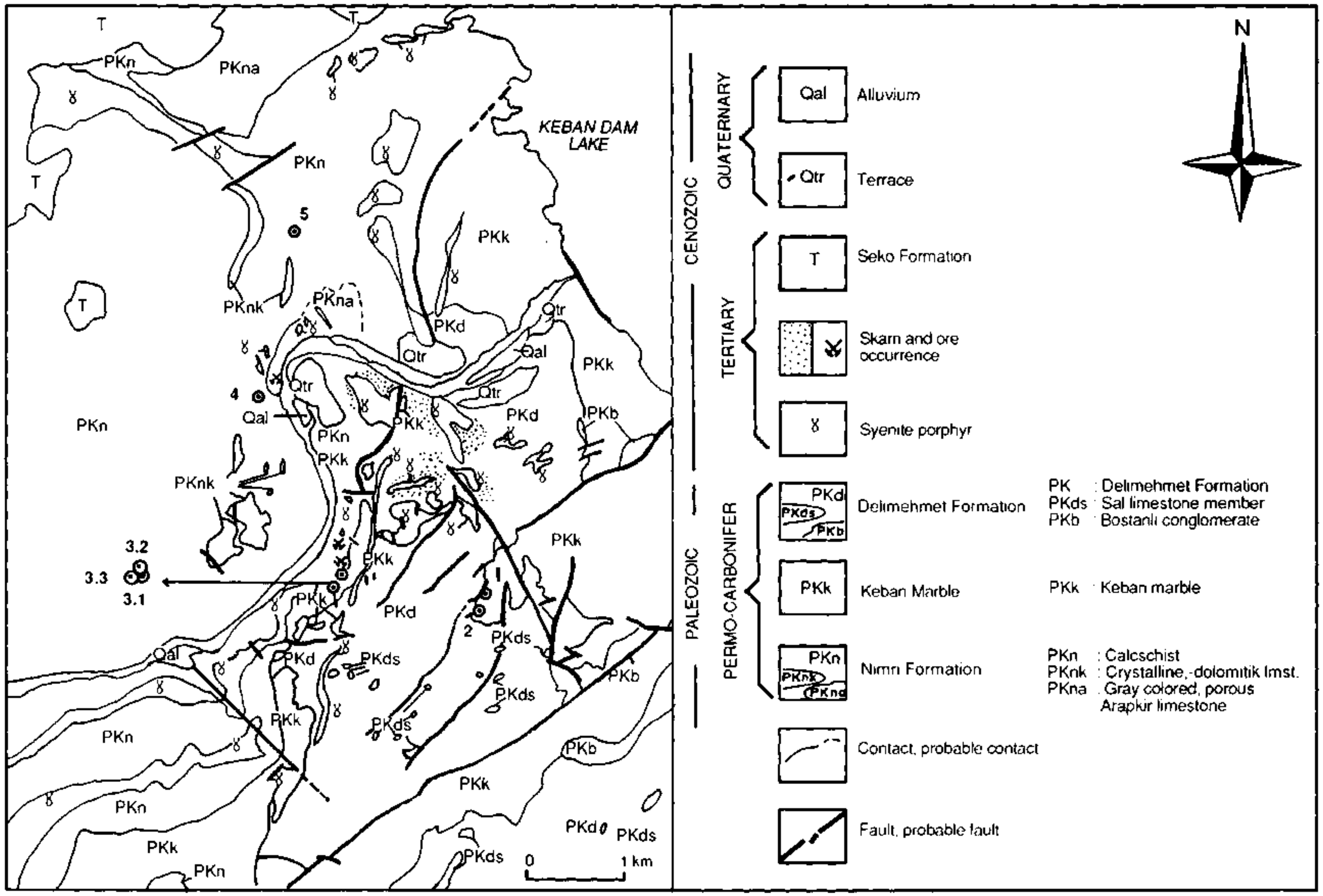

Fig. 4- Geological map of Keban and its environs and location map of sample groups which are chemically analysed (sample groups and their numbers: 1. Group: AKY. 5,7; 1' Group: AKF. 1;2. Group: AKY. 39'; 3.1. Group: AKF. 19, 21, 22; 3.2. Group: AKF. 8, 9, 12, 14, 16; 3.3. Group: AKF 17; 4. Group: AKY: AKY. 30, 31, 34, 35; 5. Group: AKB 4, 5, 8).

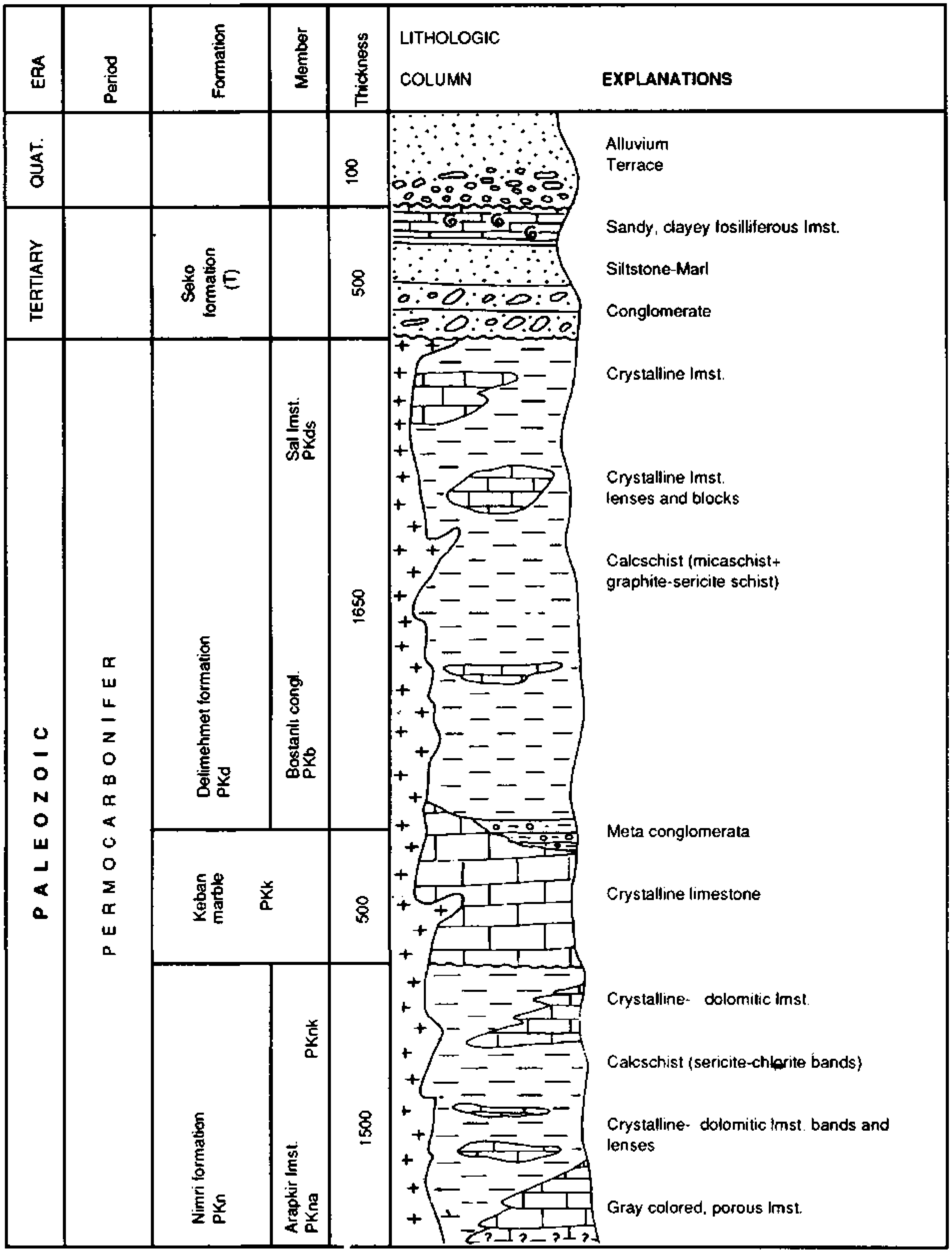

Fig. 5 - Generalized column section of studied area.

nant Irthology of Nimri formation, composed predominantly bf carbonate minerals, plagioclases, quartz and, at some horizons, of sericite, graphite, chlorite and opaque minerals. Showing lateral and vertical transitions to calcschists, crystalline limestones with decreasing amounts of dolomite crystals towards their upper outcrops in Nimri formation. In some places, sericite flakes, quartz, plagioclase and opaque minerals and also enrichments with iron and manganese minerals are observed within this lithology. Crystalline limestones display the characteristics of spatially dolomite bearing crystalline limestones or dolomitic limestones.

Keban marbles are pinkish-white colored, fractured and crached, brecaated looking and composed of equgranular, medium grained calcite crystals with deformation twinnings. At the contacts of Keban marbles formed with Delimehmet formation, increasing amounts of feldspar, quartz, chlorite, sericite and, in some places, graphite minerals, are determined.

Delimehmet formation, which is characterized by calcschists, lies above the Keban marbles, while in some places, Bostanlı conglomerate lies between those lithologies. Calcschists are represented by graphite, sericite, quartz, feldspar and chlorite. Lens shaped Sal limestone member is separated from this formation and contains fain grained quartz minerals spatially.

Magmatic rocks, which intrude all these units, consist of porphyric syenite porphyry dominated by sanidines and ortoclases. Contact metamorphic minerals of garnets and epidotes are observed at the contacts between syenite porphyries and calcschists and marbles. Additionally, syenite porphyries are subjected to the sericitic, argillic and chloritic type of alteration.

## POSITION AND MINERALOGY OF ORE

Ore horizons in a thickness of 0,5 to 2 meters are observed concordant to the layers of crystalline and dolomitic limestones of Nimri formations. These horizons are scattered on an approximately 8 km$^2$, region within the studied area and are found in underground mining activities especially between the elevations of 730-795 meters. Primary ore mineral occurrences, which are transformed from rhodochrosite, of psilomelane and pyrolusite and, in addition, fine grained pyrites are located in ore bearing horizons (Photos 1, 2 and 3). Psilomelane is also found as kidneylike, gel textured open fillings in the cracks. Pyrites constitute fine grained or medium grained, zoned pseudomorphs in the rocks. Both types of pyrite are replaced by limonite which can also be observed as gel textures in the cracks. Chalcopyrite, pyrite, sphalerite, pyrrhotite and molybdenite representing the late stages are determined in addition to the above mentioned minerals.

Mineralizations within Keban marbles form either small lenses in thicknesses of 2-20 meters or big lenses in a thickness of 20-50 meters. White, gray and brown colored sections caused by different mineral assemblages are distinguished in the mineralizations. Carbonaceous, sulphidic and oxidic ore mineral varieties representing different mineral paragenesis are determined in these sections.

Predominantly zinc carbonates (smithsonite) and lead carbonates (cerucite) form carbonaceous ore minerals within the carbonate rocks. A very small amount of galenite and sphalerite is also found in these rocks. Grinocoid and sphalerite inclusions are determined in kidney, grapelike textured smithsonites. Limonites are developed in the crackes of smithsonites (Photos 4, 5, 6).

Galenite, sphalerite, pyrite, Chalcopyrite, marcasite and arsenopyrite constitute the main sulfidic ore minerals in the Keban marbles. While pyrites and arsenopyrites accumulate in the same places, it is determined that the chalcopyrites are converted into bornite, neodigenite, chalcocite and covelline. High and low temperature types are observed in galenites and sphalerites. Low temperature types of those are characterized by geled textures.

Goethite and lepidocrocite with pyrite relicts are determined as oxidic ore minerals in the Keban marbles. In addition, Chalcopyrite, hematite, magnetite, rutile, anatase and chloritized augite are found in small amounts of detritic constituents in the grayish, brownish sections of Keban marbles.

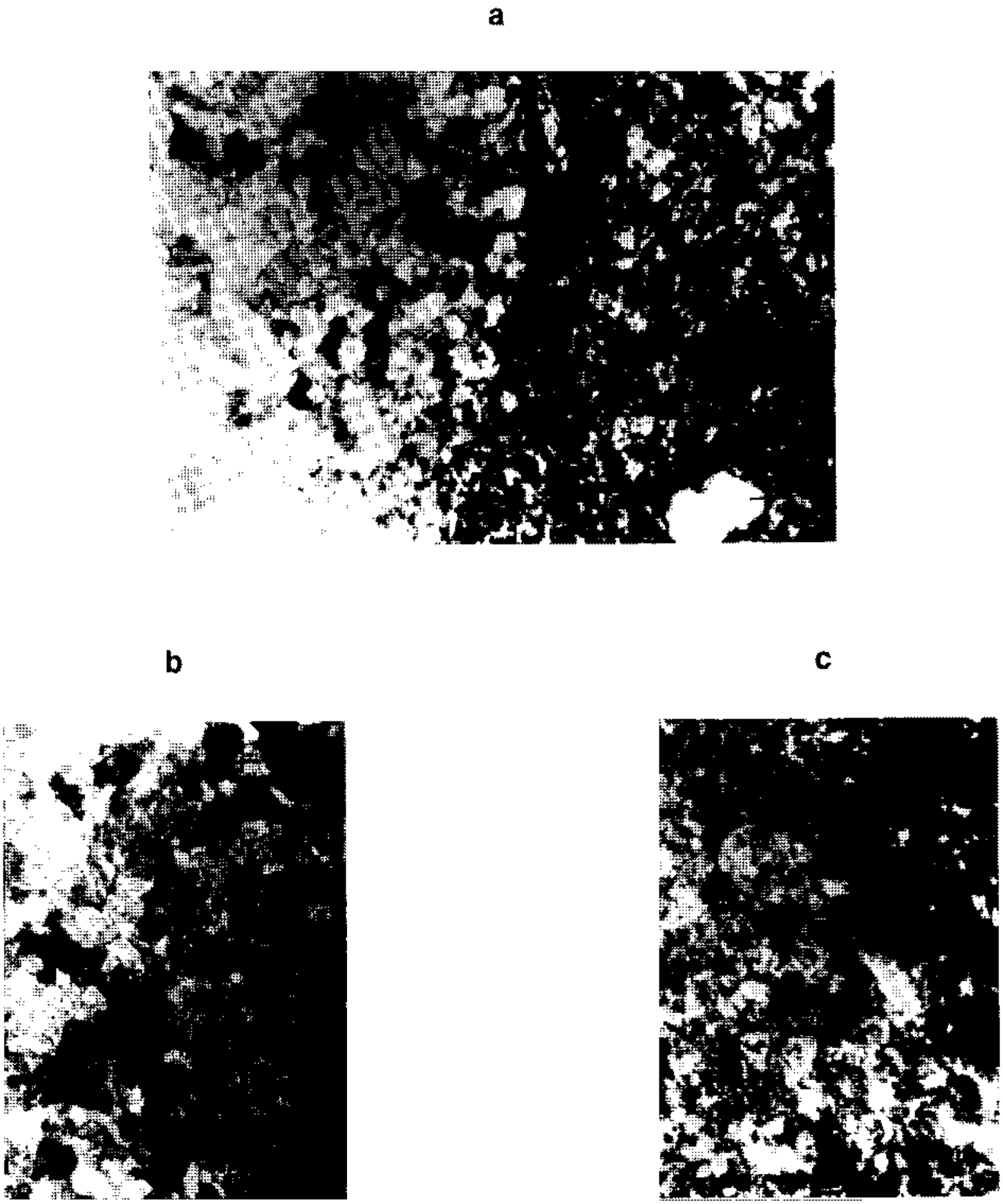

Photo 1 - Sections in crystalline-, dolomitic limestone
a) rich in calcite and manganese minerals, b) filled by calcite, c) filled by dolomite, mangan oxide minerals and a small amount of quartz
(cross nicols, X 63)

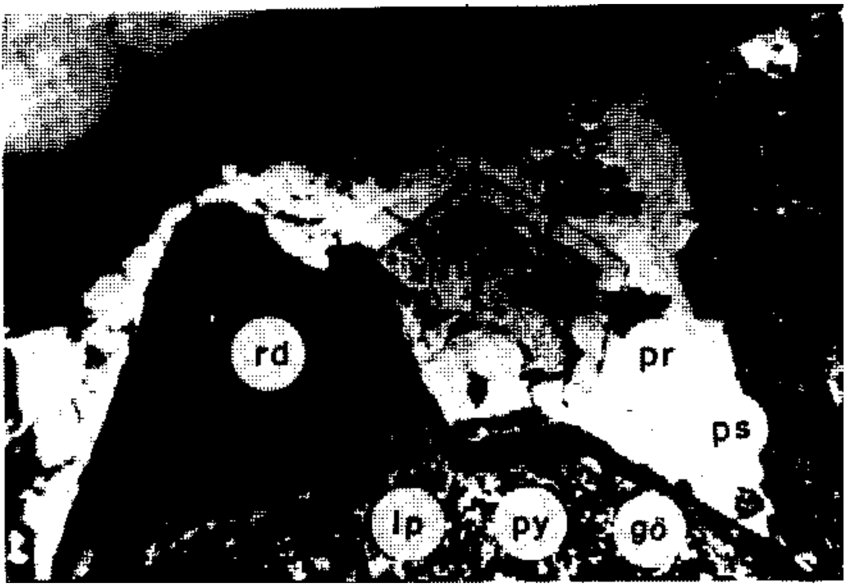

Photo 2 - Rhodocrocite (rd) replaced by pyroluzite (pr) and psilomelane (ps), pyrite (py) replaced by lepidocrocite (lp) and goethite (go) occurrences in crystalline-, dolomitic limestone, (X 420, in oil).

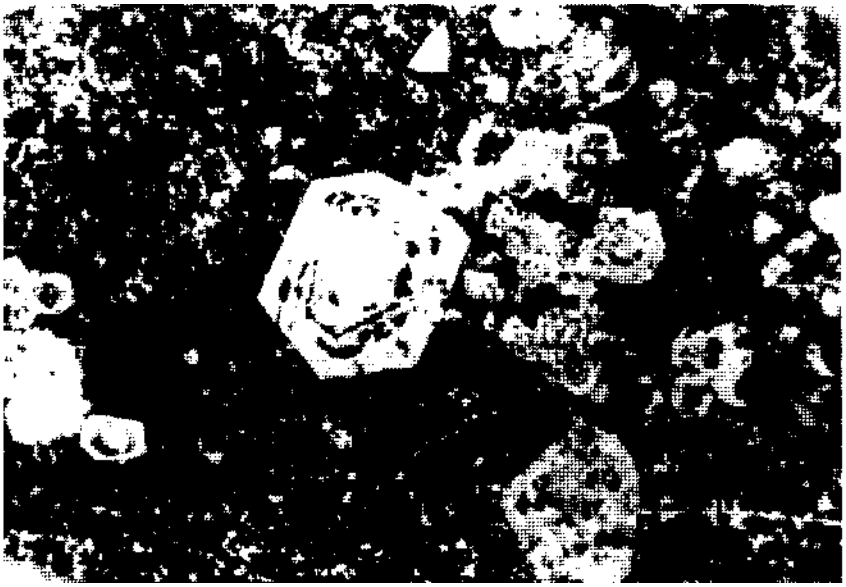

Photo 3 - Pyrite pseudomorphs replaced by limonite in crystalline, dolomitic limestone (X 420, in oil).

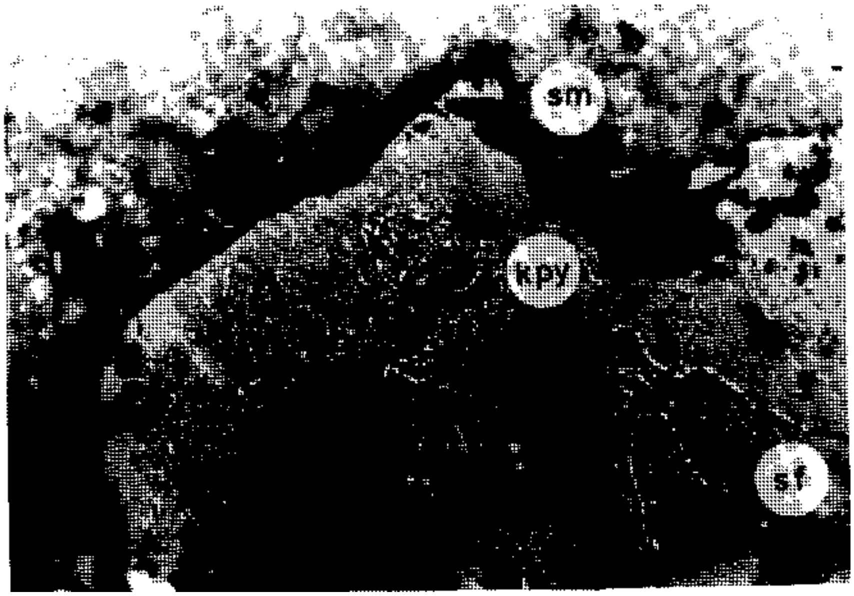

Photo 4 - Carbonate ores in Keban marbles. Smithsonite (sm), sphalerite (sf) and chalcopyrite (kpy) exolutions in sphalerite (X 420, in oil).

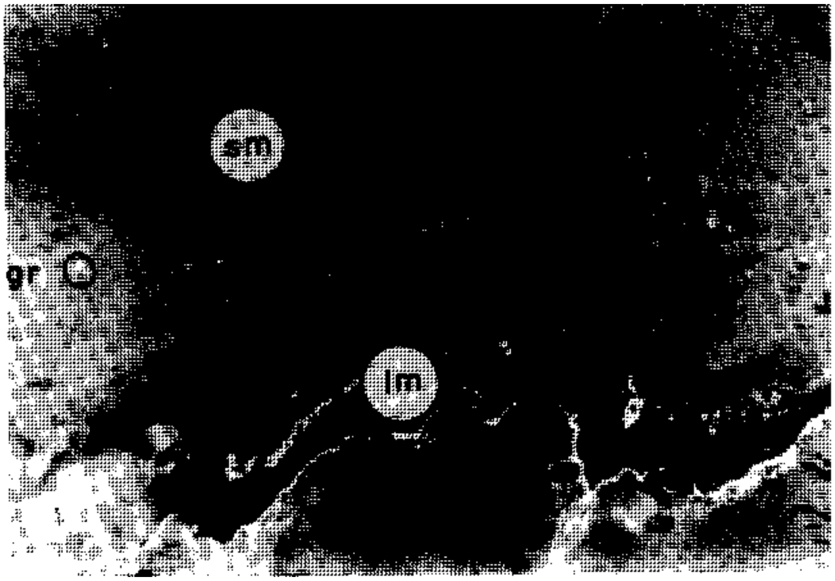

Photo 5 - Carbonate ores in Keban marbles. Grinocoid (gr) drops bearing smithsonite (sm) and limonite (lm) occurrences (X 420, in oil).

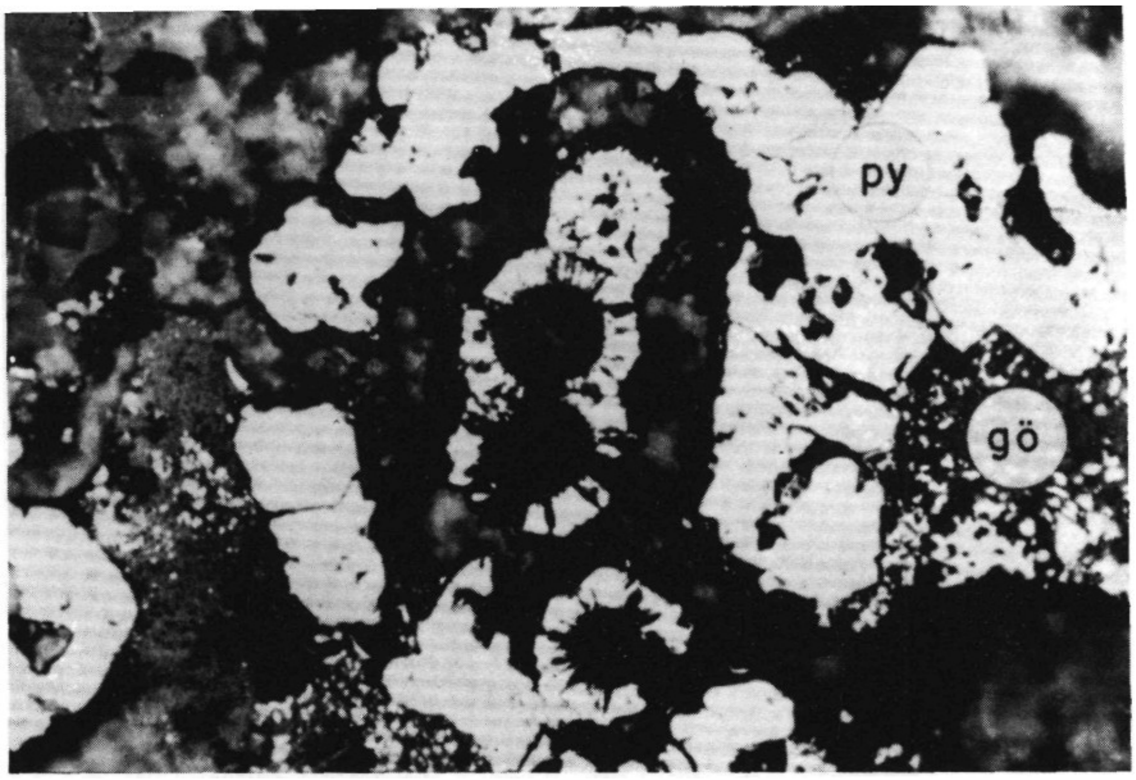

Photo 6 - Carbonate ores in Keban marbles. Goethite (go) and gel-radial pyrite (py) occurrences (X 420, in oil).

Delimehmet formation is rather poor for ore minerals and only pyrites and limonites occur in this formation.

Enrichments with ore minerals are spatially observed at the contacts of syenite porphyries with the country rocks.

## GEOCHEMISTRY AND GEOSTATISTICS

Ore and host rock samples, collected from Keban area, are chemically analyzed at Etibank laboratories. The results of these chemical analyses are shown in Table 1 and the lower and upper limits of all geochemical data are listed in Table 2.

Dolomitic limestone levels of Nimri formation are the oldest units in the area, which contain Pb-and Zn concentrations. However, low PbO and ZnO values are characteristics of these units.

Carbonate type ores within the Keban marbles are Ca, Mg, Mn, Fe, Pb and Zn carbonate minerals, which are later replaced by oxide minerals. Sulphide ores in Keban marbles are characterized by high Mn, Fe, Pb and Zn rates and high clay contents. Iron cap formations of Keban marbles show Fe and Al enrichments of surficial oxidation conditions.

Hydrothermal formations in Nimri formation, which show different features from all above mentioned mineralization bearing levels, are represented by phlogopite and quartz and high $K_2O$ rates are evident.

Relations of various elements with each other in all samples are graphically represented in Figure 6 and distribution relationships of Pb and Zn elements versus Ca, Mg, Al and Si are shown at Table 3. In this table Ca and Mg are the main components of carbonate minerals and Al and Si of clay minerals. Pb and Zn elements exhibit decreasing relationships with carbonate minerals (i.e. Ca and Mg components) and increasing relationships with clay minerals (i. e. Al components). Variable distribution relationship of Pb and Zn elements with Si of clay minerals is caused by the mobile character of Si element against secondary events. According to these results, the decrease of Pb and Zn element contents with the increase of carbonates, and increase of the same contents with the increase of clays on the one hand, and on the other the increase of carbonates against decreasing clays in the environment, all suggest a gradationally sedimentation of Pb and Zn elements with clays and carbonates.

**Table 1 - The results of chemical analyses of ore and country rock samples collected around Keban, realized at Etibank Laboratories (Yılmaz, 1991 for analytical methods)**

| UNIT | SAMPLE NR. | MARK | % $SiO_2$ | % $Al_2O_3$ | % CaO | % FeO* | % $K_2O$ | % MgO | % MnO | % $Na_2O$ | % ZnO | % PbO | % KK | TOTAL | Ba (ppm) | Sr (ppm) | Ag (ppm) | Cd (ppm) | Cu (ppm) | Ni (ppm) | Co (ppm) | EXPLANATIONS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KEBAN MARBLES | 1 | AKF-1 | 1.86 | 1.98 | 41.66 | 0.77 | 0.040 | 9.14 | 1.12 | 0.168 | 0.31 | 0.19 | 39.80 | 97.038 | 2000 | 400 | ND | ND | ND | 60 | 40 | KEBAN MARBLE |
| | 13 | AKY-5 | 1.79 | 2.85 | 41.90 | 0.14 | 0.030 | 9.75 | 0.24 | 0.138 | 0.09 | 0.03 | 40.33 | 97.288 | 900 | 700 | ND | ND | ND | ND | ND | |
| | 16 | AKY-7 | 1.92 | 0.96 | 48.80 | 0.18 | 0.043 | 3.35 | 0.61 | 0.837 | 0.06 | 0.05 | 42.00 | 98.81 | 2000 | 400 | ND | ND | 100 | ND | ND | |
| | 15 | AKY-39' | 6.80 | 12.41 | 0.04 | 70.29 | 0.063 | 0.56 | 0.76 | 0.174 | 0.06 | 0.88 | 7.20 | 99.237 | 400 | 600 | 103 | ND | 1100 | 60 | 100 | IRON CAP OF KEBAN MARBLE |
| | 7 | AKF-19 | 1.76 | 13.43 | 11.28 | 23.31 | 0.042 | 1.67 | 1.86 | 0.208 | 39.41 | 4.49 | 1.28 | 98.74 | 300 | 100 | 290 | 1600 | 300 | ND | ND | CARBONATE TYPE ORE |
| | 8 | AKF-21 | 1.86 | 10.22 | 12.36 | 19.15 | 0.045 | 1.91 | 1.78 | 0.140 | 44.08 | 0.74 | 3.57 | 95.855 | 900 | 800 | ND | 200 | ND | ND | ND | |
| | 9 | AKF-22 | 2.00 | 9.69 | 10.44 | 22.78 | 0.025 | 1.41 | 1.51 | 0.101 | 43.04 | 0.71 | 3.15 | 94.856 | 700 | 200 | 10 | 800 | 100 | ND | ND | |
| | 2 | AKF-8 | 12.40 | 14.75 | 0.64 | 36.98 | 0.054 | 2.75 | 0.43 | 0.220 | 3.73 | 2.88 | 18.59 | 93.424 | 400 | 700 | 2850 | ND | 7100 | 80 | 60 | SULPHIDE TYPE ORE |
| | 3 | AKF-9 | 14.75 | 12.27 | 1.48 | 41.01 | 0.049 | 0.20 | 2.36 | 0.140 | 0.62 | 4.13 | 17.43 | 94.439 | 700 | 300 | 395 | ND | 1900 | 80 | 60 | |
| | 4 | AKF-12 | 17.84 | 32.56 | 1.68 | 9.11 | 0.051 | 0.07 | 0.46 | 0.202 | 7.47 | 13.62 | 9.91 | 92.973 | 800 | 400 | 2050 | 200 | 1000 | ND | ND | |
| | 5 | AKF-14 | 21.70 | 22.91 | 1.30 | 20.63 | 0.024 | 0.07 | 0.83 | 0.119 | 7.26 | 15.62 | 6.77 | 97.233 | 500 | 300 | 1575 | 200 | 1100 | ND | ND | |
| | 6 | AKF-16 | 16.40 | 21.45 | 1.20 | 21.50 | 0.052 | 0.20 | 1.29 | 0.216 | 15.25 | 5.74 | 8.39 | 91.688 | 400 | 600 | 1250 | 400 | 1100 | ND | ND | |
| | 14 | AKF-17 | 0.50 | 20.96 | 7.70 | 12.32 | 0.027 | 1.31 | 3.24 | 0.163 | 23.85 | 27.47 | 0.72 | 98.26 | 800 | 800 | 2000 | 400 | 1600 | ND | ND | COMPLEX TYPE ORE |
| NIMRI FORM. | 10 | AKB-4 | 2.70 | 6.77 | 38.02 | 2.15 | 1.255 | 8.19 | 1.64 | 0.321 | 0.16 | 0.68 | 29.97 | 91.856 | 800 | 300 | 10 | ND | 200 | ND | ND | HYDROTHERMAL OCCURRENCES IN NİMRİ FORM. |
| | 11 | AKB-5 | 10.96 | 8.40 | 35.84 | 2.79 | 1.265 | 0.73 | 1.41 | 0.168 | 0.15 | 0.09 | 29.36 | 91.163 | 900 | 600 | ND | ND | 300 | ND | ND | |
| | 12 | AKB-8 | 3.18 | 6.51 | 42.64 | 1.34 | 1.305 | 1.21 | 1.38 | 0.410 | 0.14 | 0.40 | 32.93 | 91.445 | 1000 | 1000 | ND | ND | 100 | ND | ND | |
| | 18 | AKY-30 | N.A. | N.A. | 30.92 | 15.87 | N.A. | N.A. | 7.49 | N.A. | 0.24 | 0.04 | 40.98 | 95.539 | ND | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | DOLOMITIC LMST. IN NİMRİ FORM. |
| | 17 | AKY-31 | N.A. | N.A. | 52.91 | 5.43 | N.A. | N.A. | 1.07 | N.A. | 0.01 | ND | 42.63 | 102.05 | ND | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | |

FeO*: Total iron, ND: Below detection limit, N.A.: Not analysed
Chemical analyses are performed on samples dried at 105° C.

Table 2 - Lower and upper limits of the results of chemical analysis given in Table 1

|  | EXPLANATIONS | NUMBER OF SAMPLES | Pb O % | Zn O % | Ca O % | Mg O % | Fe O* % | Mn O % | KK % | $Al_2O_3$ % | $SiO_2$ % | $Na_2O$ % | $K_2O$ % | Ba ppm | Sr ppm | Ag ppm | Cd ppm | Cu ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KEBAN MARBLE | KEBAN MARBLE IRON CAP | 1 | 6800 ppm | 600 ppm | 0.0 | 0.6 | 70.3 | 0.8 | 7.2 | 12.4 | 6.8 | 0.2 | 0.1 | 400 | 600 | 103 | ND | 1100 |
|  | KEBAN MARBLE COMPLEX TYPE ORE | 1 | 27.5 | 23.9 | 7.7 | 1.3 | 12.3 | 3.2 | 0.7 | 21.0 | 0. 5 | 0.2 | 0.0 | 800 | 800 | 2000 | 400 | 1600 |
|  | KEBAN MARBLE SULPHIDE TYPE ORE | 5 | 2.9-15.6 | 0.6-15.3 | 0.6-1.7 | 0.1-2.8 | 9.1-41.0 | 0.4-2.4 | 6.8-18. 6 | 12. 3-32.6 | 12. 4-21. 7 | 0. 1-0.2 | 0.1 | 400-800 | 300-700 | 395-2850 | 200-400 | 1000-7100 |
|  | KEBAN MARBLE CARBONATE TYPE ORE | 3 | 0.7-4.5 | 39.4-44.1 | 10.4-12.4 | 1.4-1.9 | 19.2-23.3 | 1.5-1.9 | 1.3-3.6 | 9. 7-13.4 | 1.8-2.0 | 0. 1-0.2 | 0. 0-0.1 | 300-900 | 100-800 | 10-290 | 200-1600 | 100-300 |
|  | KEBAN MARBLE | 3 | 300-1900 ppm | 600-3100 ppm | 41.7-48.8 | 3.4-9.8 | 0.1-0.8 | 0.2-1.1 | 39.8-42.0 | 1.0-2.9 | 1.8-1.9 | 0. 1-0.8 | 0. 0 | 900-2000 | 400-700 | ND | ND | ND-100 |
| NIMRI FORM. | NIMRI FORMATION DOLOMITIC LIMESTONE | 2 | 400 ppm | 100-2400 ppm | 30.9-52.9 | N.A. | 5.4-15.9 | 1.1-7.5 | 41.0-42.6 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
|  | NIMRI FORMATION HYDROTHERMAL OCCURRENCES | 3 | 900-6800 ppm | 1400-1600 ppm | 35.8-42.6 | 0.7-8.2 | 1.3-2.8 | 1.4-1.6 | 29. 4-32.9 | 6.5-8.4 | 2. 7-11.0 | 0. 2-0.4 | 1.3 | 800-1000 | 300-1000 | ND -10 | ND | 100-300 |

Abbrevations like in Table 1.

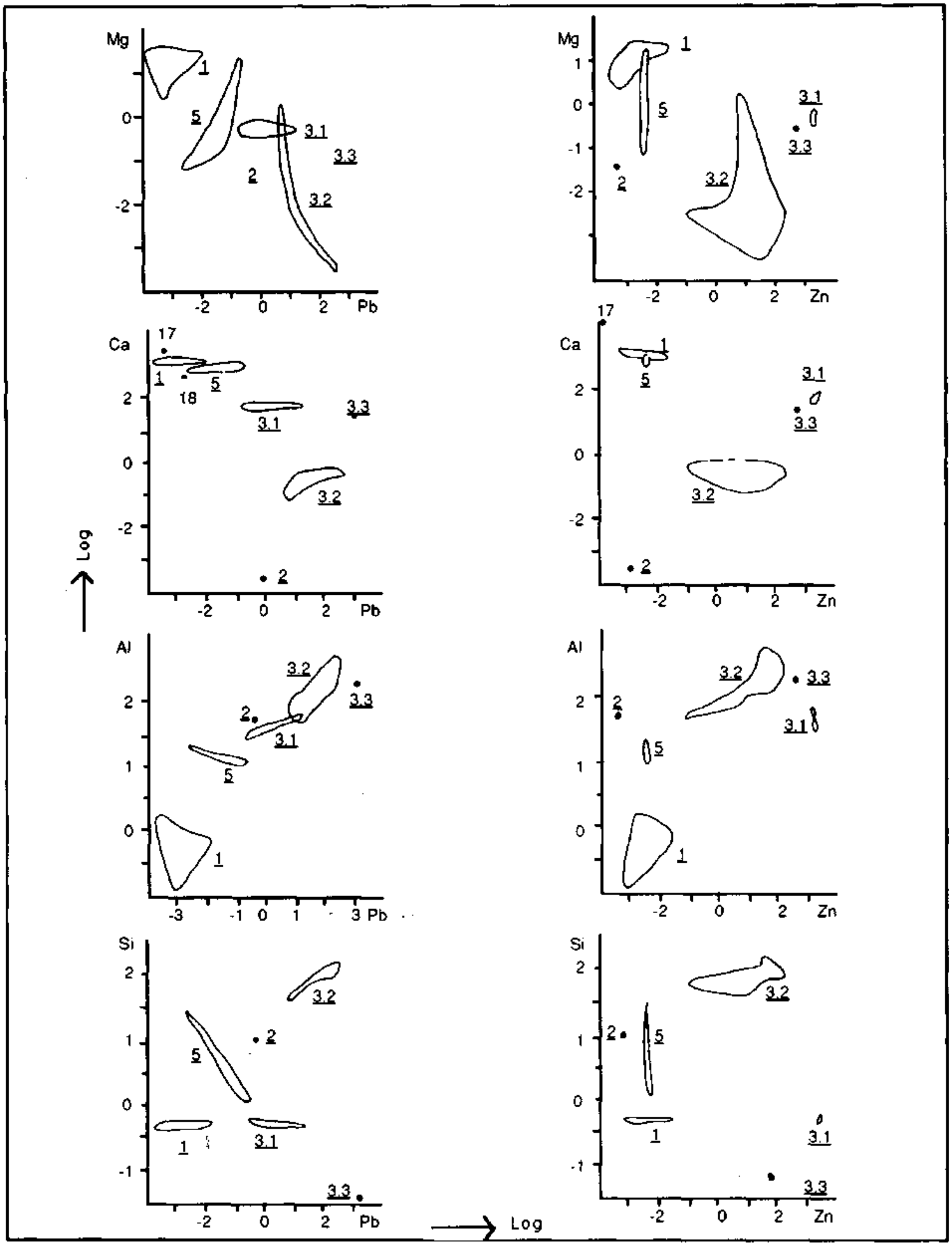

Fig. 6 - Logarithmic distribution relationship of Pb and Zn elements versus Mg, Ca, Al and Si in all groups. (see figure-4 for sample groups and Table 6 for 17. and 18. samples).

**Table 3 - Relationship of Pb and Zn elements versus Ca, Mg, Al and Si in all groups**

| METALS | CARBONATE | | CLAY | |
|---|---|---|---|---|
| | Ca | Mg | Al | Si |
| Pb | decreasing relationship | decreasing relationship | increasing relationship | variable relationship |
| Zn | decreasing relationship | decreasing relationship | increasing relationship | variable relationship |

Keban marbles and two group of carbonate ores within them are summarized as one group under the name of carbonate samples and sulphide samples in Keban marbles as one group under the name of sulphide samples and these new two groups are subjected to correlation analyses (i.e. cluster and factor analyses). Element associations are listed in Table 4 and Table 5.

1. Group with high positive correlation (Al, Fe, Mn, Zn, Pb, Cd and Ag) observed in total rock analyses (Table 4) belonging to carbonate samples exhibits association of metals with clay minerals. Nonexistence of Si element in this group is supposed to be caused by decomposition of aluminum silicates and thus, while Si is removed from the environment, aluminium hydroxide becomes enriched. 2. Group with high positive correlation belonging to carbonate samples (Ca, Mg) is a result of existence of dolomite formation in the environment and necessity of dolomite formation in the environment and necessity of dolomite during ore formation process.

1. Group with medium positive correlation (Al, Fe, Mn, Zn, Pb, Cd, Ag and Cu) belonging to carbonate samples differ from 1. Group of high positive correlation with the addition of only Cu element to the same association. On the contrary, 2. Group with medium positive correlation (Ca, Mg, Sr, Ba, Co, Ni, Si, Na and K) contains Ca, Mg, Sr, and Ba elements, which are expected to take place in carbonates, and Co and Ni elements (probably in pyrite), which are expected to be enriched in clay minerals and Si element, which becomes free during the process of aluminium hydroxide from clay minerals. Na and K, here, are probably related with clay composition.

**Table 4 - Element groups and associations determined from carbonate samples of Keban marbles**

CARBONATE SAMPLES

High Positive Correlation ($r > +0.75$)

1. Group: Al, Fe, Mn, Zn, Pb, Cd, Ag
2. Group: Ca, Mg

Middle Positive Correlation ($+0.34 < r < +0.75$)

1. Group: Al, Fe, Mn, Zn, Pb, Cd, Ag, Cu
2. Group: Ca, Mg, Sr, Ba, Co, Ni, Si, Na, K

High Negative Correlation ($r < -0.70$)

| 1. Group | 2. Group |
|---|---|
| Al, Fe, Mn, Zn, Pb, Cd, Ag, Cu | Ca, Mg, Sr, Ba |

Middle Negative Correlation ($-0.35 > r > -0.70$)

| 1. Group | 2. Group |
|---|---|
| Al, Fe, Mn, Zn, Pb, Cd, Ag, Cu | Ca, Mg, Sr, Ba, Co, Ni, Si, Na |

**Table 5 - Element groups and associations determined from sulphide samples of Keban marbles**

SULPHIDE SAMPLES

High Positive Correlation (r > + 0.75)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 1. | Group: | Al, | Zn, | Pb, | Cd, | Ca, | Si, | Ba |
| 2. | Group: | Mg, | Sr, | Co, | Ni, | Na, | K. | Cu |

Middle Positive Correlation (+ 0.34 <r <+ 0.75)

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Group: | Al, | Zn, | Pb, | Cd, | Ca, | Si, | Ba, | Mn | |
| 2. | Group: | Mg, | Sr, | Co, | Ni. | Na, | K. | Cu, | Fe, | Ag |

High Negative Correlation (r<- 0.70)

| | |
|---|---|
| Al, Pb, Cd, Ca, Si | Mg, Sr, Co, Ni, K, Cu, Fe, |
| 1. Group: | 2 Group |

Middle Negative Correlation ( - 0.40 > r > - 0.70)

| | |
|---|---|
| Al, Pb, Cd, Ca, Si, Zn, Ba, Mn | Mg, Sr, Co, Ni, K, Cu, Fe, Na, Ag |
| 1. Group | 2 Group |

High negative correlation are determined in two groups of carbonate samples. 1. Group consisting of Al, Fe, Mn, Zn, Pb, Cd, Ag and Cu, points out metals and aluminium hydroxide, 2. Group, consisting of Ca, Mg, Sr and Ba elements, indicates dolomite formation.

What is important here is that these two groups show a highly positive correlation in themselves but a highly negative correlation between each other. The elements of the first and second groups represent a highly positive correlation both in and between each bther but the elements of these two groups show a highly negative correlation reciprocally. This situation displays that the elements of both groups exhibit two different behaviourial features separately. On the other hand, a highly negative correlation (relationship) between two groups expresses that these two different geological events are in the necessity of being the products of developments which belong to the same environment and are directly related with each other (This geological event here is expressed with the word, association). Under the light of these opinions, high negative correlation relationship of carbonate samples suggests that the clays accompany metals on the one hand and on the other, for the sedimentation or crystallization (i.e. stabilization) of metal ions, dolomite (and/or dissolution of calcite) is needed for the equilibrium of the environment from the physicochemical point of view.

A medium negative correlation (relationship) of carbonate samples shows Al, Fe, Mn, Zn, Pb, Cd, Ag and Cu association versus Ca, Mg, Sr, Ba, Si, Na, Co and Ni association. The first association (group) reflects metals and aluminium hydroxide and second one, most heavily, dolomite and silica occurrences. As a result of decomposition of clays, aluminium hydroxide and silica become free and these two components take their place in different physicochemical environments, it means that aluminium hydroxide and metals are enriched and dissolved Si separates from the environment or with a different-geostatistical expression, Si supplies association with the elements of second group.

The above explanation of carbonate samples in Table 4 puts forward the below interpretation:

Metal rich carbonate samples in Keban marbles are the isochronal components of an environment in which clay and carbonates precipitate together. Metal concentrations together with clay components in the environment become enriched probably with the dissolution of carbonates rich in metal ions. It is suggested that the dolomitization of dissolved carbonates are closely related with separation processes of metals from dissolved carbonates.

Original results observed from total rock analyses of sulphide samples (Table 5), symbolize the complex and hard interpretable associations observed in the formation,of sulphide mineralizations.

The results of the interpretation efforts of elements of two different group, which correlate positively with each other, and element associations of two groups, which correlate negatively with each other, can be summarized as follows:

The difficulty in the interpretation of association of both Al, Pb, Cd, Ca, Si versus Mg, Sr, Co, Ni, K, Cu and Fe with high negative correlation of sulphides necessitates the cointerpretation of associations of medium negative correlation (Al, Pb, Cd, Ca, Si, Ba, Mn versus Mg, Sr, Co, Ni, K, Cu, Fe, Na and Ag). Therefore, with the useful of elements of coexisting minerals, which accompany to ore minerals and are expected to reflect the environmental conditions, it can be realized that they will interpretate together with ore minerals as a whole.

At the association of Al, Pb, Cd, Ca, Si, Zn, Ba and Mn comprising of the first group, Pb, Zn and Ca are used for the formation of galenite and sphalerite, Al and Si for clay minerals and Ca, Ba and Mn for relatively low amounts of carbonate minerals which are associated with clay minerals.

To the contrary of the association of Ca to Mg in carbonate samples, in this group Ca is not accompanied by Mg and so Mg takes place in the second group. Again, Al and Si observed in carbonate samples are localized in different groups. These elements, found together in the first in sulphides, exhibit gnother difference. That is, an environment occurs, which differs from the one that is formed probably dissolution of metal carbonates and observed in carbonate samples, in this environment, conditions of almost no dissolution of carbonates, no dolomitization and destabilization of clay minerals become important.

Thus, an occurrence form of sulphides in the compositions of directly primary formation of galenite and sphalerite becomes more and more visible.

Fe, Cu, Co, Ni, Ag indicate particularly pyrite and chalcopyrite as sulphide minerals in the association of Mg, Sr, Co, Ni, K, Cu, Fe, Na and Ag which consist of the second group. Very low amount of Mg, Sr, Na and K point out probably the sea water (?). Thus, the second group element association suggests that particularly pyrite and chalcopyrite rich sulphide mineralizations are most probably affected by seawater.

The above explanation of sulphide samples in Table 5 suggests the below interpretation:

Studies, carried out on sulphide samples in Keban marbles, point out that galenite and sphalerite and also pyrite and chalcopyrite are the main constituents of sulphides and these two mineral associations occurred successively. The occurrences of less carbonate but abundant clay components and probably effects of seawater can not be ignored in such an environment where an occurrence form expressed by different mineral phases may become original.

## SYNTHESIS

Different genetic interpretation basing on the analyses carried out on ore and host rocks of Keban and its mineralizations around, which are classified as directly related with granitoids in earlier studies, and especially geochemical-geostatistical studies, urges detailed evaluation of this subject. For this reason, four samples (AKY-30, 31, 34 and 35) taken from the carbonate levels which are observed concordant to the schists basing on field observation and which take place in Nimri formation, which is the oldest unit in this region, are analyzed at MTA laboratories.

Chemical analyses, XRD and DTA results of these samples are totally listed in Table 6.

**Table 6 - The results of chemical, X-ray diffraction and DTA analyses of four samples in Nimri formation made in MTA Laboratories. (Yılmaz, 1991 for analytical methods)**

| RATIOS | ELEMENTS | AKY. 31 | AKY. 30 | AKY. 34 | AKY. 35 |
|---|---|---|---|---|---|
| % | $SiO_2$ | 1. 40 | 5. 00 | 1. 00 | 2. 40 |
| | $Al_2O_3$ | 1. 20 | 3. 15 | 4. 60 | 3. 55 |
| | $Fe_2O_3$ | 1. 55 | 12. 63 | 14. 61 | 34. 48 |
| | MnO | 2. 03 | 10. 04 | 30. 19 | 26. 05 |
| | $TiO_2$ | 0. 07 | 0. 07 | 0. 03 | 0. 02 |
| | CaO | 49. 50 | 29. 90 | 14. 40 | 8. 10 |
| | MgO | 1. 90 | 6. 00 | 0. 15 | 0. 55 |
| | $Na_2O$ | < 0. 10 | 0. 20 | 0. 15 | 0. 10 |
| | $K_2O$ | 0. 15 | 0. 20 | 0. 15 | 0. 15 |
| | $P_2O_5$ | 0. 10 | 0. 10 | 0. 10 | 0. 10 |
| | A. Z. | 41. 70 | 31. 45 | | 16. 50 |
| | BaO | | | 2. 40 | 1. 10 |
| | $SO_3$ | | | 20. 00 | |
| | $H_2O^-$ | | | 11. 94 | |
| | S | 0. 03 | 0. 17 | | 0. 41 |
| | Pb | 0. 06 | 0. 02 | 0. 26 | 3. 34 |
| | Zn | 0. 05 | 0. 03 | 1. 13 | 2. 35 |
| | **TOTAL** | 99. 74 | 98. 96 | 101. 11 | 99. 20 |
| | BaO | < 0. 02 | < 0. 02 | | |
| | Zr | < 0. 01 | < 0. 01 | < 0. 01 | < 0. 01 |
| | Sr | < 0. 10 | < 0. 10 | < 0. 10 | < 0. 10 |
| ppb | Au | 11 | 150 | 17 | 11 |
| ppm | Ag | 6. 2 | 5. 4 | 28. 2 | 162 |
| | As | 37 | 380 | 150 | 173 |
| | Sn | < 50 | < 50 | < 50 | < 50 |
| | Co | < 10 | < 10 | < 10 | < 10 |
| | Cr | < 10 | 13 | 22 | 25 |
| | Cu | < 10 | 24 | 33 | 33 |
| | Ni | < 10 | < 10 | < 10 | < 10 |
| | V | < 10 | 15 | 19 | 20 |
| | Cd | < 10 | < 10 | 57 | 10 |
| | Sb | < 20 | < 20 | 31 | 200 |
| | Bi | < 50 | < 50 | < 50 | < 50 |
| | Rb | | | | |
| XRD RESULTS | | Calcite (abundant)<br>Dolomite (rare)<br>Rhodocrocite? (rare)<br>Quartz (rare)<br>Clay minerals (rare) | Manganocalcite ? - Dolomite (abund.)<br>Calcite (less)<br>Quartz (very rare) | Gypsum (abundant)<br>Clay min. (rare)<br>Dolomite (rare)<br>Calcite (very rare)<br>Barite ? (very rare) | Goethite ? (abund. ?)<br>Quartz (very rare ?)<br>Hematite ? (abund. ?)<br>Clay min. (very rare) (sericite ?)<br>Amorph substance in diphractogram |
| DTA RESULTS | | Calcite | Dolomite<br>Calcite | Gypsum<br>Calcite ?<br>Clay min (Kaolinite ?)<br>Gypsite ? or Goethite | Goethite ?<br>Calcite ?<br>Clay min. ? |

The sample AKY-31 displays a lot of similarities to those samples which are collected mineralogically from crystalline-dolomitic limestone lithologies of Nimri formation. Micro photographs of those samples are illustrated in Photo-la in general and Photo 1b in detail. For example, carbonate part is formed by totally recrystallized, clamped calcite mosaic.

The sample AKY-30 shows a great similarity to those samples which are collected again from crystalline-, dolomitic limestones of Nimri formation. Those samples represent transition character between the samples in Photo 1 a in general and Photo 1 c in detail, and Photo 7.

Photo 7 - Solution breccia observed in crystalline-, dolomitic limestone (cross nicols. X 40).

In general sense, the sample AKY-30 has brecciated texture and coarse and medium grained dolomitic crystals are observed in less fine dolomite and ore mineral matrix. In thin sections made at the other parts of this sample, clamped, recrystallized calcite mosaic with transition to brecciated texture in some places (solution breccia) are also observed like sample AKY-31. The latter case can be schematized, like in Figure 7, in micro size.

Some feldspar (alkali feldspar?) and quartz (volcanic quartz?) mineral particles are also found in some places of solution breccia. Dolomite particles as fine dolomite sand become rich in this breccia and brecciated structure exhibit transition to fractured structure. Dolomite particles together with sericite flakes consist weak laminations in ores.

The sample AKY-34 displays another composition different from the two samples mentioned above. In this sample, gypsum minerals are widespread. Calcites in dissolved sections show radial growth structures in abundance. These structures are heavily developed in spaces and gypsum crystals accompany them. Thus, calcite and gypsum phases are met repeatedly in these spaces. Ore emplacement are also accompany to those phases.

The sample AKY-35 is microscopically characterized by enrichment of ore phases with the rock fragments represented by sericite, very rare gypsum crystals and calcite fillings in some places.

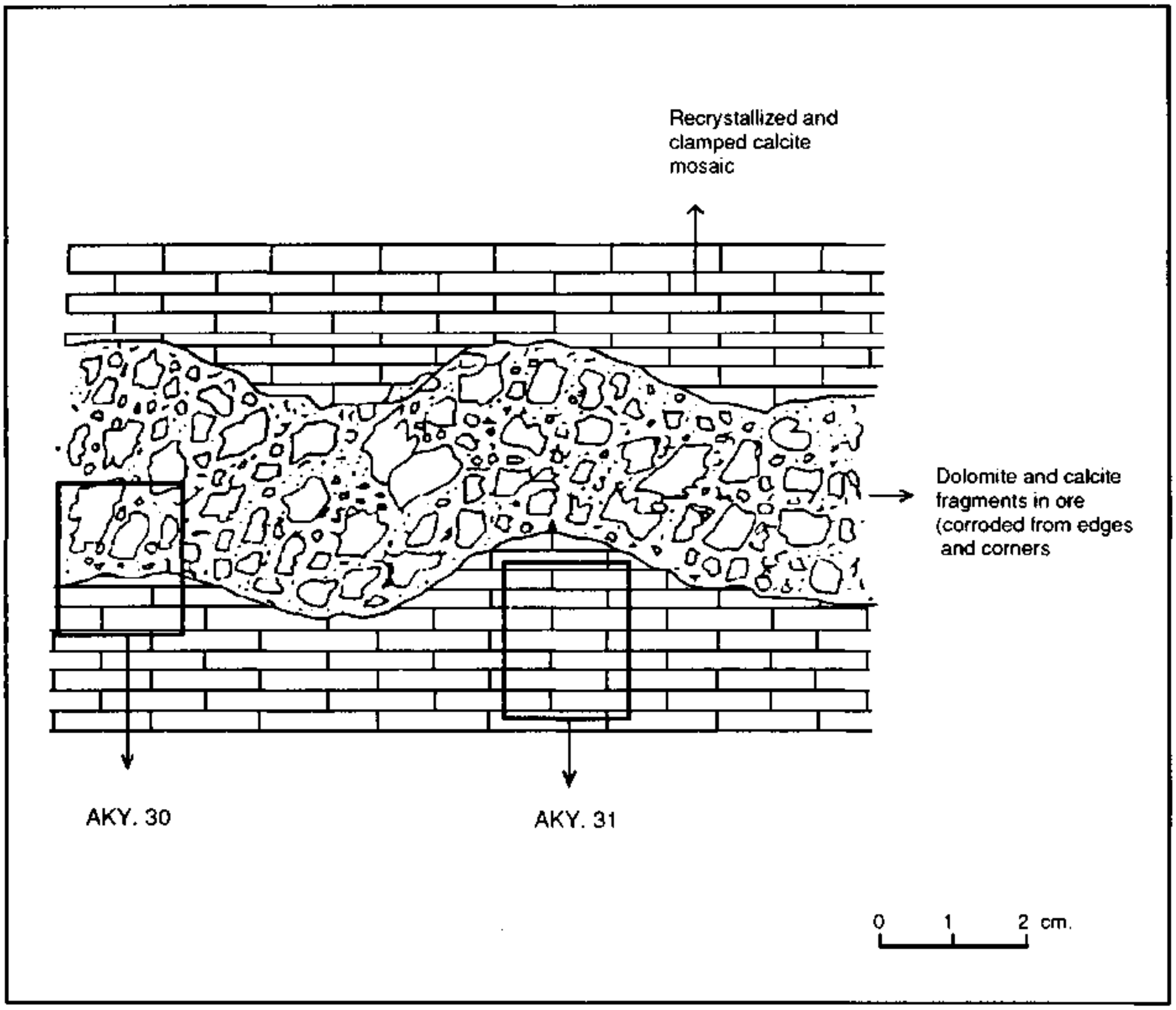

Fig. 7- Schematized transition from massive structure to breccious structure in crystalline-, dolomitic limestone (symbolized places of studied two samples: AKY. 30, 31).

The sample AKY-31 formed totally calcite minerals with 49.50 % CaO and 41.70 % ignition loss rates shows very close coincident with the carbonates of Nimri formation. MgO ratio is 1.90 % and dolomitization is almost absent. The interesting point of this sample is that it contains 500 ppm Zn and 600 ppm Pb. MnO and $Fe_2O_3$ draw attention with high rates of 10.04 % and 12.63 % respectively, in the analyses of the sample AKY-30. MgO ratio is 6.00 %. Secondary psilomelane and pyrolusite minerals are often observed on the rhodochrosite minerals at the microscopic investigations of this sample (like in photo 1 a, c and photo 2). 200 ppm Pb and 300 ppm Zn are found in the same sample.

In the samples AKY-34 an AKY-35, Pb rates range from 2600 ppm to 3.34 % and Zn rates from 1.13 % to 2.35 %. Fe and Mn rates are quite high in these samples. Metal contents of these samples are enriched by secondary processes, which is verified by thin-and *ore* section studies. It is observed in the samples taken from levels concordant to the schists in Nimri formation as a result of detailed geochemical studies that carbonate phases which contain Pb, Zn, Fe and Mn metals are replaced by metal rich phases by late secondary processes. As an original result, the existence of Fe and Mn elements in high ratios in carbonate facies must be emphasized.

## DISCUSSION

In order to introduce a discussion on the origin of lead-zinc mineralizations of Keban and its environs, a short compilation of general features for Mississippi Valley Type (MVT) and Exhalative Sedimentary Type (SEDEX) deposits, based on literature, appears to be useful.

MVT deposits are characterized by nonexistence of magmatic rocks at their vicinity, lateral extension over hunders of square kilometers, thicknesses of less than 100 meters and quite simple mineralogy. Especially, galenite with low silver and sphalerite with low iron content, fluorite, barite, rare pyrite and marcasite are the main components. Although vein type mineralizations, fracture fillings related with folding and solution and collapse breccia fillings generally form the important type of deposition, mineralizations show developments as unconformities of layered, stratabound replacement type in sedimentary host rocks which are consisted of generally dolomite or dolomitized limestones. Solution activities are widespread. Most of the mineralizations occur as open space fillings in solution breccias, however some are certainly as replacements. Mineralizations are settled at the sides of large sedimanter basins, shallow depth and structurally passive, anorogenic regions. Although, these mineralizations are discussed as syngenetic, diagenetic and epigenetic occurrences from genetical point of view (Ohle, 1959; Synder, 1967; Anderson, 1975; Roedder, 1976; Vaughan and Craig, 1978; Giordano and Barnes, 1981; Sverjensky, 1984; Guilbert and Park, 1986 and Pratt, 1990), they are considered in the class of "suspicious deposits related with magmatism" according to the criters of Synder, 1967 (Guilbert and Park, 1986).

SEDEX type deposits usually occur in sedimentary host rocks of Precambrian and Paleozoic age. The mineralogy with pervasive galenite and sphalerite and abundant of pyrite and pyrotite are typical. Silver and iron contents are high. Mineral zoning is their typical characteristic. Deposition both in deep sea and in shallow water sediments is possible. Syngenetic and diagenetic Pb-Zn mineralizations in carboriate and shale host rocks are especially investigated. Although no direct relation is established between mineralizations and volcanism, most of the deposits occur either at the same age of some regional volcanic activities or in basins in which significant amounts of volcanic material are located especially at the lower parts of stratigraphic sequence. Sediment hosted statiform Cu-Pb-Zn deposits differ from volcanogenic massive sulphide deposits in nonexistence of associating volcanism. Compared by MVT deposits, these stratiform deposits have significant differences as early mineralization time due to basic sediment deposition, more conformity with the basic sediments, higher iron sulphides and Ag ratios and contents (Gustafson and Williams, 1981; Large, 1981; Lydon, 1983; Edwards and Atkinson, 1986).

Important parameters related with both types are given in Table 7.

**Table 7 - Significant parameters of MVT and SEDEX-Type deposits (Generalized after Pratt, 1990)**

| PARAMETERS | MVT | SEDEX |
|---|---|---|
| Temperature | ~ 100 - 150° C | ~ 100 - 300° C |
| Salinity | 1 - 3 m. | 0. 5 - 3 m. |
| p H | 4 - 7 | 3. 5 - 6 |
| $\epsilon S$ | $10^{-3}$ - $10^{-2}$ m. | $10^{-3}$ - $10^{-2}$ m. |
| $fO_2$ | $10^{-58}$ - $10^{-46}$ | $10^{-50}$ - $10^{-38}$ |
| Metals | Zn,Pb, Fe, Cu, Ba | Zn, Fe, Pb, Cu, Ba, Ag |
| Tonnage | $< 10^{6}$ - $> 10^{6}$ t | $> 10^{7}$ t |
| Grade | 4 - 6 % Zn + Pb | 10 - 15 % Zn + Pb |

In general sense, genetical critic between SEDEX and MVT deposits includes the discussion of syngenetic and epigenetic formation type. Ore bearing solutions (metals and/or sulphides) enter the environment, whether during the formation of primary minerals of rocks of after their formation, constitute the focus of the genetic interpretation problems. According to the recent studies, modern findings lead to the opinions that the feeding channels of syngenetic occurrences (SEDEX) characterize the epigenetic occurrences (MVT). Thus, these two type occurrence are related with each other and a combination of continuity due to both formation mechanisms and characteristics are presented by various authors (Gustafson and Williams, 1981; Pratt, 1990).

Some basic features determined related with Pb-Zn mineralizations of Keban and its vicinity and are given as follows:

a) According to the field observations, mineralizations are stratiform type deposits concordant to the host rocks in Nimri formation.

b) Existence of abundant primary rhodocrocite minerals in concordant mineralizations of Nimri formation.

c) In the calcites of primary carbonate minerals of Nimri formation, 500 and 600 ppm Zn and Pb, respectively, are determined due to the geochemical studies (Table 6).

d) As a result of geostatistical evaluations, metals belonging to the mineralizations of Nimri formation and Keban marbles show strong evidence for the associations of graditionally precipitation and zoning between carbonates and clays (Table 3, 4 and 5).

e) Ore formation as matrix of solution breccias and breccias especially in ore bearing level of Nimri formation.

Thus, some of the above mentioned important criteria related with Pb-Zn mineralizations of Keban and its environs exhibits similar and/or common character with SEDEX type, though the others with MVT deposits.

## INTERPRETATION

Most of the samples are distributed in exhalative sedimentary (SEDEX) type field, when the chemical analyses are plotted on Fe, Pb, Zn diagram illustrated in Figure 8. If the same analytical results are transported on Cu, Ag, Pb+Zn diagram (Figure 9), again most of them are located very close to the SEDEX field, but their character of high Ag contents predominates.

Carbonate samples in Keban marbles (Number 7, 8 and 9 in Figure 8) show attractive similarities to those of Cafana (Malatya) Zn-Fe-Pb-Ba mineralizations of sedimentary type. Although Cafana mineralizations have a transition type feature between exhalative sedimentary (SEDEX) type and Mississippi Valley Type (MVT) (Pratt, 1990), Keban occurrence exhibit a great tendency toward SEDEX type.

The most important geochemical characteristic, observed in Keban mineralizations, is high amounts of Fe, Mn and Ag which emphasize close similarities to SEDEX type.

It is a fact that genetically related volcanism in field studies, which is expected to form source rock for ore development, doesn't exist locally, and this isn't handled sufficiently. But, being aware of the existence of volcanism (metadiabase) within the Permian units in a large regional geology will be able to create important evidence for the establishment and further strengthening of the relation between the data to be gained from further studies, and the above interpretation.

## CONCLUSIONS

Primary ores of Keban Pb-Zn mineralizations in Nimri formation, whether they are classified as SEDEX type or MVT, are not skarn type mineralizations directly related with granitoids.

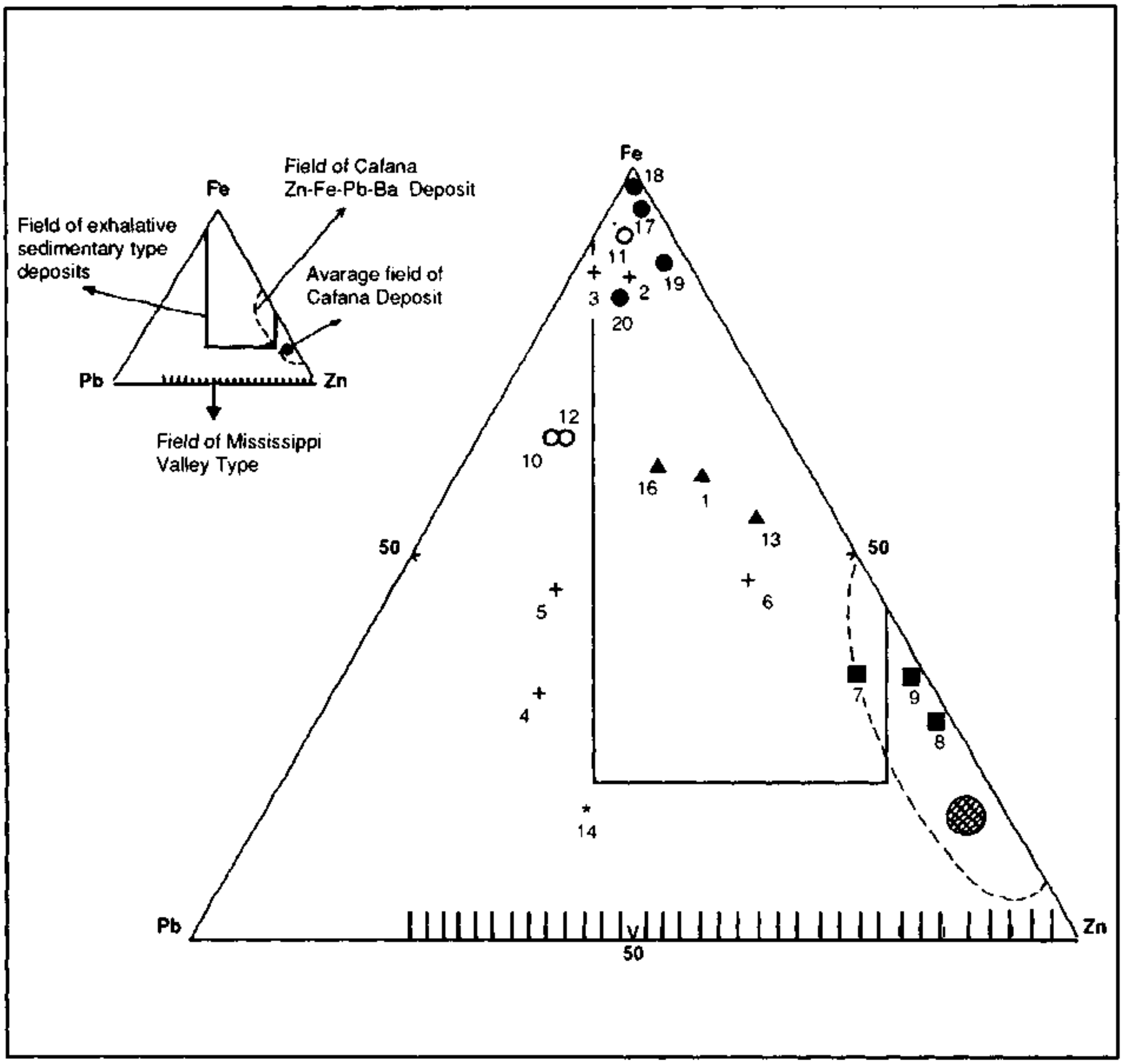

Fig. 8 - Locations in Pb-Fe-Zn triangle diagram of Keban (Elazığ) lead-zinc occurrences. (Numbers like in Table-1, but samples 17, 18, 19 and 20 are equal to AKY 31, 30, 34 and 35 in Table- 6, respectively. Related fields are taken from Gustafson and Williams, 1981; Lydon, 1983; Sangster, 1983 and Pratt, 1990).

Metals, belonging to primary ores, could be more enriched later as a result of mobilization with the effect of granitoids. On the other hand, minerals, formed by mobilizing metal bearing solutions, are located together with skarn minerals in some places and, on the other, minerals, belonging to granitoids, are added to the primary ore minerals. Primary ores contain different mineral paragenesis with lower temperatures than skarn type mineralizations.

Mobilizations related with metamorphism and/or granitoid impact and enrichment processes caused by weathering are out of the study. The emphasize has been given on the origin of primary ores which constitute source for mineralizations in the region.

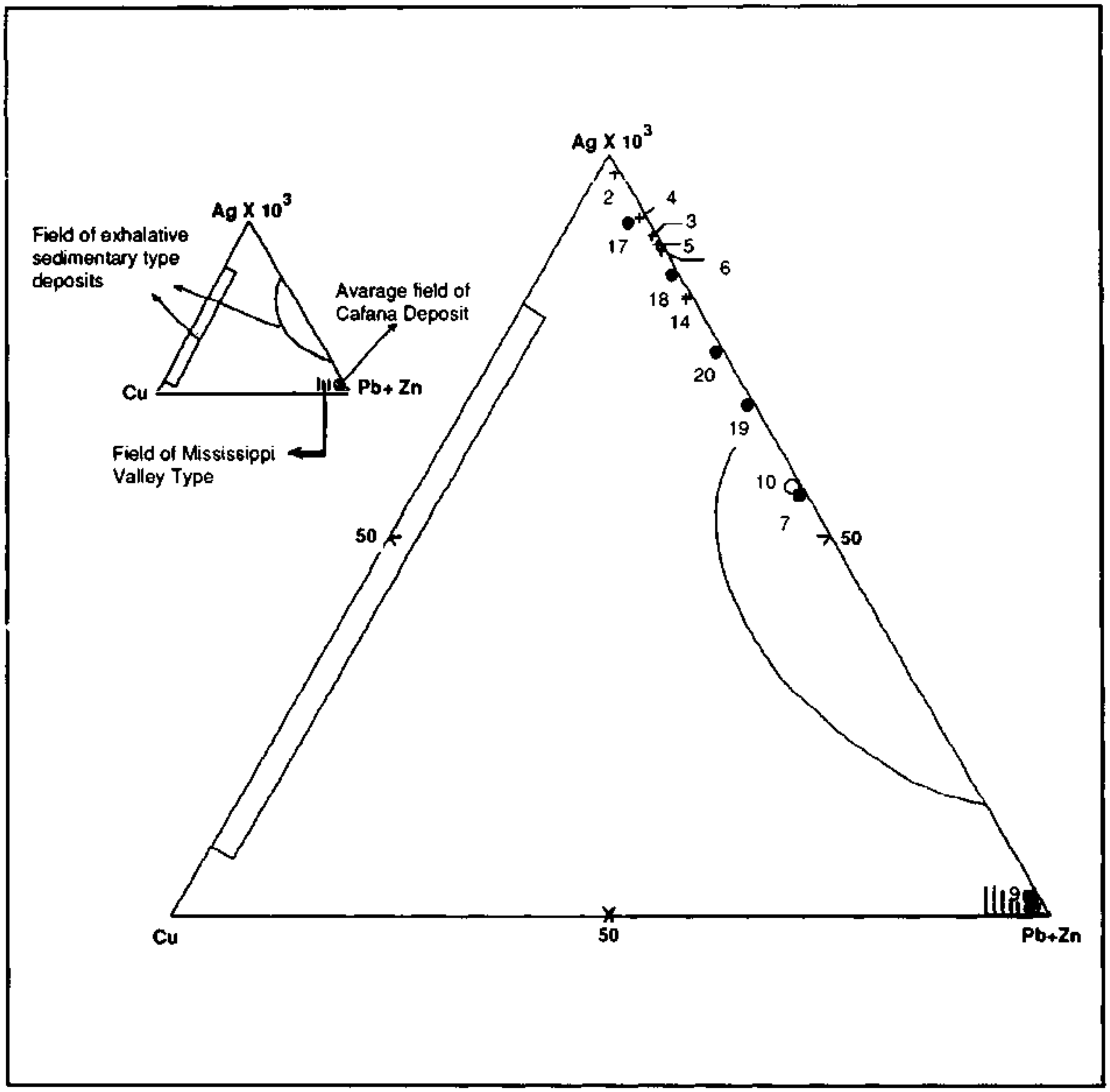

Fig. 9 - Locations in Cu, AgX$10^3$ and Pb+Zn triangle diagram of Keban (Elazığ) lead-zinc occurrences (symbols and references are like in Figure 8).

Investigation and separation of mineralizations, belonging to granitoids, which accompany to primary ores, with detailed efforts during next field studies are very important in order to avoid the complexity of planned studies.

The subject of the-origin of the lithologies in the Nimri formation and their relations to Keban marble are left open as an important problem which should later be taken into account.

This paper presents a preliminary study of the understanding of the primary origin of ores at Keban district with the discussion of the problems related with this subject. The insufficient data basis of this study leads to the necessity of much more data in order to understand the problems. This type of studies may result in the highlighting of the agenda of the. revrtalization of mining activities again, which are gradually terminating at present.

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