Occurrences of Saplıca alunite deposits and properties in Sebinkarahisar (Giresun, NE Turkey) volcanic field

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Alunite occurrences, related to Upper Cretaceous volcanic rocks of acid to intermediate composition from northern part of Sebinkarahisar, located in the south of eastern Black Sea region of Pontid provenance. Upper Cretaceous aged volcanic rocks of the Sebinkarahisar volcanic field intruded by same aged acidic plutonics and unconformably overlie Palaeozoic volcanic and ophiolitic rocks (Ayan and Dora, 1993). Eocene and Miocene-Palaeocene volcanic and sedimentary rocks covers the other volcanic and plutonic.

Saplıca volcanites remarkably altered by hydrothermal solutions and comprises of riyolite, dacite, and andesite lava and pyroclastics. Most of the replacement alunite deposits are located in the low hills of volcanic complexes and abundant in the centre of the advanced argillic alteration zone develops laterally outward from the alunite border.

Most of the large replacement of alunite deposits in Sebinkarahisar volcanic field are located around the periphery of Saplıca volcanites and contain alunite and kaolinite, quartz$\pm$opal$\pm$cristobalite. Illite and most rarely illite-smectite present whereas hematite, jarosite are common and more prevalent than pyrite and baryte or gypsum. Alunite replacement are generally observed in generally fault and contact zones and partly in pyroclastics by means of porosity controlled. Some spring waters are seen especially in these locations. pH of these waters are between 2.33 to 6.40. Vertically, the replacement of these deposits vary systematically downward from a quartzose cap though hematitic, jarositic, alunitic and finally propylitic zones. The complete sequence can be observed at only a few deposits but can be pieced together from several different localities (Celik and Karakaya, 1997).

The replacement alunite forms massive, fine-grained, white to light pink aggregates that are slightly denser than less altered rocks. Most of the texture of the pre-existing volcanic rock has been obliterated in the alunite zone, but relict clasts and phenocrysts can be discerned wither the transition zone to kaolinite. In thin section, the alunite appears as an interlocking and granular quartz with minor hematite dust. Small, spotty patches of jarosite occur near the top of alunite zone. Most of the pre-existing volcanic rock here is replaced by an alunite-quartz mixture, but jarosite adds a golden-brown colour.

Hematite forms a characteristic bright red stain on incompletely altered volcanic that contain some alunite and quartz. The hematite is distributed vertically as a band above the jarosite zone and beneath the flooded silica zone.

Dense granular quartz of the flooded zone forms the top of the alteration sequence and commonly forms resistant caps on the highly coloured hills. Much of the quartz is massive, light grey has a concoidal fracture, and contains brecciated fragments of volcanic rocks. It consist of a microgranular intergrowth of quartz crystal locally containing disseminated aggregates of fine-grained hematite crystals.

X-ray diffraction analysis of these samples showed that distribution of most trace elements correlates inversely with alunite content. K_2O and Al_2O_3 in alunite deposits are found to be in the range 6.50% to 7.30% and 15.70% to 46.80%, respectively. Size of alunite crystals ranges between 2μm and 15μm. Alunite crystals sometimes observed in euhedral shape and especially amorphous crystals contain much silica (between 5% to 12%) in EDS analysis. The trace elements Y, Sc, Mo, Cr, Co, Ni, Zn to be mobile in acid aqueous systems and are nearly absent in the zone. In the surrounding kaolinitic envelope, on the other hand, these elements are present in background or slightly higher concentrations. In illitic zone, Rb and Sr content are high. Barium is highest close to the alunite zone because of the relative insolubility of baryte in acid solutions.

The spring waters are meteoric in origin and they are rich in especially SO_4, K, Al and partly Fe, Si and Ca. The colour of waters varies colourless to brown and around the source of waters recent mineralization such as gypsum, alunite, goetite are determined.

Overlying zones characterised in turn by dominant jarosite, hematite and quartz apparently formed by reactions with progressively modified upward-moving solutions containing silica, iron, and other bases released from the underlying volcanic rocks during alunitization.

The change upward from alunite to jarosite indicates a change from Al to Fe^{3+} in the sulphate mineral structure, probably reflecting a decrease in the solubility of Al relative to Fe^{3+} with increasing pH and f_{O_2} (Cunningham *et al.*, 1984). The change upward from alunite-jarosite to hematite was caused by a decrease in sulphate activity and an increase in f_{O_2} because of the abundance of atmospheric oxygen near the ground surface. The silica in solution from the alunitized rocks was transported upward and was deposited at or near ground surface.

Sufficient H_2S could have present in the thermal system to be oxidized at the water table to H_2SO_4, causing the low pH environment necessary to form alunite (Wirsching *et al.*, 1990, Pirajno, 1992). By reaction with strongly acid primary solution rich in SO_4^{2-} in acidic to intermediate rocks is almost entirely altered opal$\pm$cristobalite along the high percolation. The resulting strongly acid solutions rich in, which mainly contains aluminium besides silicon and other elements causes extensive alteration to opal + alunite in the adjoining rocks. After saturation of alunite and alunite precipitated with silica minerals then alunite consumed and solution of pH become high kaolinite precipitated with or without alunite. The alunites are enriched ^{34}S and they are hypogenetic in origin (Özgenç, 1993). These results also supported that requisite amount of H_2SO_4 must have been generated by a magmatic hydrothermal environments.

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