Mg-mineral occurrences in the Central Anatolian Neogene intra-cratonic basins related to neotectonic regime: an example from Kangal basin, Sivas, Turkey

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Introduction

The Sivas Basin is one of the Central Anatolian intracontinental basins. It has been formed on two main continental tectonic units, namely the Tauride-Anatolide Platform in the south and the Central Anatolian Crystalline Complex in the north, during latest Cretaceous-Early Paleocene by the closure of the northern branch of the Neo-Tethys Ocean (e.g., Sengör & Yilmaz, 1981; Görür et al., 1998) or as the result of a tensional-transtensional regime (e.g., Yilmaz, 1994; Poisson et al., 1996; Dirik et al., 1999). After the evolution of the post-collisional peripheral foreland type of Sivas Basin has been completed during the Middle Miocene by the closure of North Neotethyan ocean and collision of the Anatolian and Arabian plates (e.g., Yilmaz, 1994; Poisson et al., 1996; Görür et al., 1998), the shallow intra-cratonic Kangal Basin developed during Middle-Late Miocene onto the Sivas Basin under the neotectonic ova regime (Sengör & Yilmaz, 1981). Kangal Basin consists of fluviatile, lacustrine and/or playa sediments of Middle Miocene-Late Pliocene age. It represents the mineralogical variations corresponding to different facies, and is surrounded by ophiolitic suite (Figure 1). This work reveals the mineralogical and geochemical features of sedimentary rocks and their diagenetic alteration products associated with coal formations and contemporaneous volcanism.

Methodology

Samples collected from each facies and source ophiolitic sequences were processed for mineralogical and petrographic such as optical microscopy and scanning electron microscopy (SEM) and chemical analysis, both major and trace elements. Whole-rock and <2 µm clay mineralogy were determined with X-ray diffractometry (XRD). Semi-quantitative analyses were carried out using an external standard method by means of mineral intensity factors related to peak intensities. Separation of clay fraction was carried out after treatment with hydrochloric acid to remove carbonates, sedimentation and centrifugation. For each clay fraction, oriented mounts were prepared by smearing the clay on the glass slides and investigated after air-drying, heating and glycolation. b parameter was calculated from 060 reflection in random powders to determine the octahedral character of I-S and smectite. Kaolin polytypes were recognized at unoriented powder patterns. High-temperature treatments of phyllosilicate minerals were conducted on a coupled differential thermal analyserthermogravimetry (DTA-TGA) analyzer. Abundances of major, minor and selected trace elements were determined by a wavelength-dispersive X-ray fluorescence spectrometry (XRF) calibrated against international rock standards. Trace and rare-earth elements analyses were carried out with inductively coupled plasma-mass spectrometry (ICP-MS).



Figure 1. The regional geological setting of the Kangal Basin (1: Cover Rock Units, 2: Kangal Basin, 3: Sivas Basin, 4: Pontide Belt, 5: Plütonic rocks, 6: Ophiolitic rocks, 7: Central Anatolian Crystalline Complex, 8: Tauride Belt, 9: Eastern Anatolian Metamorphic Rocks, 10: Southeastern Anatolian Autocthon, NAF: North Anatolian Fault, EAF: East Anatolian Fault (Modified from Bingöl, 1989).

Results

The sedimentary sequence in the Kangal basin is divided into three facies from bottom to top according to the main lithological characteristics and deposition environments: (1) Fluviolacustrine clay facies, (2) Playa coaly tuffite facies, (3) Lacustrine carbonate facies. The first facies is vertical and grades laterally to the second facies, and each facies is locally made up of sub-facies (Figure 2).



Figure 2. Geodynamic reconstruction for the Kangal Basin and setting of the worked facies (1: Basement Rock Units, 2: Sivas Basin Rock Units, 3-7: Kangal Basin Rock Units, 3-4: Fluviolacustrine clay facies, 3: Channel filling clastics, 4: Clay, 5-6: Playa coaly tuffite facies, 5: Tuffit, 6: Coal beams, 7: Lacutrine carbonate facies.

Fluviolacustrine clay facies is composed of red-brown to green claystone and marl with subordinate channel filling sandstones and conglomerates, and carbonate rock intercalations with a total thickness of about 200 m. The main minerals found in the clayey-calcareous rocks are clay minerals, calcite, aragonite, dolomite, magnesite, and to a lesser extent, quartz, opal-A, opal-CT and feldspar. Local mineralogical differences are frequently seen in some places of the basin. Clay fractions consist of palygorskite, serpentine, smectite, sepiolite, illite and chlorite in order of abundance. Mixed-layer chlorite-smectite (C-S), illite-smectite (I-S) and talc are also detected in some samples. SEM study in a sample containing dolomite + palygorskite showed that palygorskite commonly occurs as mats of interwoven fibers coating dolomite rhombs and in the matrixes.

There is little tetrahedral Al for Si, but high octahedral Fe for Mg and Al substitutions in the palygorskite: $(AI_{1.37}Fe^{+3}_{0.79}Cr_{0.01}Mg_{1.72})(Si_{7.96}AI_{0.04})O_{20}(OH)_2(OH_2)_4(Ca_{0.01}Na_{0.03}K_{0.04})$. Smectites have dioctahedral composition at the central part of the basin, but locally trioctahedral composition at the margin of the basin nearer to ophiolites that can be called as Al-Fe sapo-

nite: $(AI_{0.27}Fe^{+3}_{0.78}Mg_{1.42})(Si_{3.60}AI_{0.40})O_{10}(OH)_2(Mg_{0.08}Ca_{0.12}Na_{0.01})$. Main mineral in the serpentinized ultramafic rocks of the source region is 1T type Mg-lizardite with the following structural formula: $(Mg_{2.90}Fe^{+3}_{0.05}Cr_{0.01}Ni_{0.01})(Si_{1.86}AI_{0.03}Fe^{+3}_{0.11})O_5(OH)_4$.

Playa coaly tuffite facies consists of four zones namely, lower coal (15 m), lower tuffite (28 m), upper coal (11 m) and upper tuffite (33 m) that can be observed only in open pits. Tuffaceous claystones bearing abundantly mollusc shells are the dominant lithology in all zones. Rhizolitic and pisolitic limestone intercalations (1-5 m) are also encountered in the upper tuffite zone.

The tuffaceous and/or coaly samples contain significant amounts of amorphous matter (10-90%), consisting of both organic matter and volcanic glass, as well as calcite, aragonite, quartz, feldspar and clay minerals. In addition, the rocks have small contents (< 10%) of, pyrite, marcasite, gypsum, and trace anhydrite, barite, witherite, dolomite, hornblende and biotite. The predominant clay minerals are kaolinite and/or smectite with less illite, chlorite, C-S and I-S, and rare palygorskite. The smectites are dioctahedral corresponding to montmorillonite: $(AI_{1.34}Fe^{+3}_{0.27}Mg_{0.39})(Si_{3.94}AI_{0.06})O_{10}(OH)_2(Mg_{0.05}Ca_{0.14}Na_{0.03}K_{0.02}).$

Lacustrine carbonate facies mainly consist of yellow to white carbonate rocks with partly clayey, cherty and/or fossiliferous (limestone, dolomite and magnesite) horizons with thickness varying from 20 to 60 m.

In all facies, volcanogenic products and clay minerals show a noticeable enrichment in the REE (Figure 3), with regard to chondrites (Boynton, 1984). Unaltered lavas and tuff show similar but more enriched patterns than clay-rich tuffites and clay minerals. REE contents are highest in the kaolinite rich samples and are depleted showing a negative Eu anomaly.



Figure 3.Chondrite-normalized REE patterns of the analysed samples.

Conclusions

In all facies, Ca and Mg transported from the surrounding rocks contributed to the formation of calcite, aragonite, Mg-calcite, dolomite and magnesite. In the smectite-free samples, sepiolites and/or palygorskites are formed from solutions with concentration of Mg ions derived from ultramafics and dolomite grains, rather than detrital phyllosilicates (Yalcin & Bozkaya, 1995, 2004), according to the following equations (1-2 for sepiolites, 3-4 for palygorskites):

 $12H_{4}SiO_{4}+16OH^{-}+8Mg^{+2} \rightarrow Mg_{8}Si_{12}O_{30}(OH)_{4}(OH_{2})_{4}.8H_{2}O+18H_{2}O (1)$ $8CaMg(CO_{3})_{2}+12H_{4}SiO_{4} \rightarrow Mg_{8}Si_{12}O_{30}(OH)_{4}(OH_{2})_{4}.8H_{2}O+16CO_{2}+2H_{2}O+16OH^{-}+8Ca^{+2} (2)$ $8H_{4}SiO_{4}+10OH^{-}+2Mg^{+2}+2(AI,Fe^{+3}) \rightarrow (AI,Fe^{+3})_{2}Mg_{2}Si_{8}O_{20}(OH)_{2}(OH_{2})_{4}.4H_{2}O+12H_{2}O (3)$ $2CaMg(CO_{3})_{2}+8H_{4}SiO_{4}+2OH^{-}+2(AI,Fe^{+3}) \rightarrow (AI,Fe^{+3})_{2}Mg_{2}Si_{8}O_{20}(OH)_{2}(OH_{2})_{4}.4H_{2}O+4CO_{2}+8H_{2}O+2Ca^{+2} (4)$

In the playa coaly tuffite facies, quartz, feldspar, rare biotite and hornblend have igneous origin. Silica, AI and Fe cations such are released during hydrolysis of pyroclastic products, mainly volcanic glass and S related to coalification, are used in the formation of clay minerals and sulfides (pyrite and marcasite) respectively. Gypsum and anhydrite associated with coal zones are diagenetic minerals. Tonstein layers contain kaolinite, derived from volcanic glass instead of feldspar. Smectite in rare bentonitic layers instead of kaolinite formed from volcanic glass due to environmental conditions such as salinity and/or alkalinity, pH, the organic material content, inflow of fresh water and clastic material (Yalcin & Gümüser, 200). The remaining silica from the hydrolysis of volcanic glass crystallized usually opal-A and partly opal-CT. These reactions are given as follows (e.g., Bohor & Triplehorn, 1993):

glass+water \rightarrow hydrated Al-silicate gel \rightarrow kaolinite or smectite+water (+cations)

 $4SiO_2.2Al_2O_3+14H_2O \rightarrow 2Al_2(OH)_6.4Si(OH)_4 \rightarrow Al_4[Si_4O_{10}](OH)_8+10H_2O$

 $8SiO_2.2AI_2O_3.MgO.Na_2O.CaO+22H_2O \rightarrow Na_2O.CaO.MgO.4AI(OH)_3.8Si(OH)_4 \rightarrow Na_2O.CaO.MgO.4AI(OH)_4 \rightarrow Na_4O.CaO.MgO.4AI(OH)_4 \rightarrow Na_4O.CaO.MgO.AAI(OH)_4 \rightarrow Na_4O.CaO.AAI(OH)_4 \rightarrow Na_4O.CaO.AAI(OH)_4 \rightarrow Na_$

(Na,Ca)(MgAl₃)[Si₈O₂₀](OH)₄.H₂O+16H₂O+6OH⁻+2(Na⁺,Ca⁺⁺)+Al⁺³

Trace or low amount of illite in some samples of all facies represent the clay-size detritus of micas. I-S has not a detrital origin in the playa coaly tuffite facies at least and the preservation of feldspars in the pyroclastic rocks suggests that I-S probably was formed from volcanic glass rather than feldspars similar to kaolinite (e.g., Yalcin & Gümüser, 2000). Chlorite and C-S developed by alteration of biotites and/or volcanic glass.

Variations in elemental concentrations of altered pyroclastics, compared to their unaltered equivalents, are related to the presence of various mineral assemblages as a result of the alteration. Mobile element contents in the altered volcanogenic materials are lower compared to tuffs depending on different degree of alteration. Trace element abundances of clay minerals seem to be controlled by the parent material and mode of formation as well as crystal structures.

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