^{40}Ar/^{39}Ar geochronology and Sr-Pb isotopic evidence of post-collisional extensional volcanism of the eastern Pontide paleo-arc, NE Turkey

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Tertiary aged post-collisional volcanics show stratigraphic, petrographic and age differences in the northern and southern zones of the eastern Pontides. The Eocene sequences in E-W direction are exposed as basin fillings in the southern zone and overlay the Upper Cretaceous and Paleocene aged units. The volcanic rocks in the Gümüşhane and Alucra areas are mainly basalt, basaltic andesite, andesite, trachyandesite and rare rhyolite-obsidien.

Petrochemically, the Gümüşhane area volcanics vary from basalt to dacite with low alkali tendency, whereas the Alucra area volcanics from basalt to basaltic-trachyandesite with high alkali tendency. The differences on the element variations of the tholeiitic-alkaline transition and calc-alkaline rocks can be explained by fractionation of clinopyroxene + hornblende + plagioclase ± magnetite ± apatite. The trace element variations show some similarities with enrichment of LILE and negative Nb, Ta and Ti anomalies. Particularly, the enrichments in LILE and a lesser extent in LREE, but the depletions in HFSE indicate that the rocks evolved from a parental magma derived from an enriched source formed by mixing of slab and asthenospheric melts. The chondrite-normalized-REE patterns of these volcanics resemble to each other and spoon-shaped with low to medium enrichment (La_N/Lu_N=2-35), indicating similar source area for the Gümüşhane and Alucra area volcanics.

The ^{40}Ar-^{39}Ar dating of the studied volcanics are between 37.7±0.2 and 44.5±0.2 Ma. The $(^{87}Sr/^{86}Sr)_i$ values of the rocks are between 0.70457 and 0.70556, and their $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ isotopic ratios range 18.59 to 18.73, 15.62 to 15.64 and 38.65 to 38.86, respectively. Pb- and Sr- isotopic ratios may imply that the rocks derived from a source region at the boundary of the mantle-crust, but the samples with low $(^{87}Sr/^{86}Sr)_i$ values (<0.705) reflect the mantle source in their origin. The increasing values of SiO_2 (wt.%), Sr (ppm) ve $(1/Sr)x10^3$ ppm^{-1} versus $(^{87}Sr/^{86}Sr)_i$ values suggest fractionational crystallisation (FC) rather than assimilation (AFC) in their evolution. Based on volcanic variety and distributions together with field and petrological data, volcanic activity in the Eocene time of the eastern Pontide is closely related to extensional tectonic regime with transtansional faults.

The role of cations versus anions in the dissolution of ionic crystals

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In growth and dissolution of binary ionic crystals, a common assumption is that the cation plays a more fundamental kinetic role than the anion. This thinking derives from the recognition that a key step in ion transfer between solid and solution involves hydration (dissolution) or dehydration (crystallization). In the case of carbonate growth, the energetic penalty of removing water from the hydration shell may impose the limiting step, particularly if the metal involved is strongly hydrated (e.g., Fe^{2+}, Mg^{2+}). Surface complexation models [e.g., 1,2] are consistent with this thinking. However, to explore this process accurately requires knowledge of the inteaction of these species with particular surface sites.

We can test these ideas with parameterized Monte Carlo calculations of dissolution reactions involving various carbonates. These models involve the full crystal lattice and are parameterized by *ab initio* and DFT calculations. This approach allows us to study the problem of how a given ion (Ca^{2+}, CO_3^{2-}) interacts at individual surface kink sites. In addition, we can investigate the role of specific metal inhibitors (Mn^{2+}, Sr^{2+}, Mg^{2+}). We will present several examples, including (1) the influence of an impurity metal on dissolution in terms of dehydration versus carbonation reactions, and (2) differences in reaction pathway during anion versus cation attachment and detachment. The tested model generates a predictive tool for dissolution kinetics of carbonate minerals.

References

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