As mobilization and accumulation in topsoils (Chalkidiki, Greece)

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The geothermal field of Chalkidiki prefecture, Northern Greece, is known as an arsenic rich region. Arsenic concentrations range from 300 to 3000 ppb in groundwater within the area. Agriculture is the first economic activity and fields are irrigated during the dry period from May to September (600 mm/yr). A soil sampling campaign conducted in 2008 found As concentrations (HNO_3 digestion) in irrigated topsoil ranging from 5 to 110 mg/kg outside the geothermal area and from 20 to 520 mg/kg inside the geothermal area. Topsoil containing more than 200 mg As/kg is in need of remediation according to intervention values reported by most of the EU countries (EUR 22805-EN, 2007). In the same area, high As concentrations, up to 690 mg/kg, were found in some limestone rocks which may represent a source for arsenic in groundwater. Core soils (50 cm depth) collected in As rich irrigated areas showed a good correlation among As and Ca along the vertical profile.

A selection of 11 soils with different As contents (low <30 mg/kg, medium 30<mg/kg<200 and high>200 mg/kg) was used for column leaching experiments. Synthetic rainwater (no As) and irrigation water (1500 ppb As) were used to simulate 10 rainfall events (50 mm each) followed by 10 irrigation events (50 mm each). The amount of As leached during the rain events varied from 0.5 % to 6.0 % of the intial amount. The amount leached is correlated with the fraction of clay, stressing the importance of the residence time of water in soil to desorb arsenic. The As adsorbed during the irrigation period (12.5 mg/kg added) ranged from 6.3-12.4 mg/kg. Soils with low As content showed almost 100% sorption capacity, but even the soil with high arsenic content could still sorb at least 50% of the As contained in the irrigation water. These results suggest that arsenic accumulates in agricultural topsoils during the summer period and that about 30% is re-mobilized during the winter rainfalls. Risks to food safety and yield are likely to increase with the build-up of As in the soil and futher investigation of the As content in agricultural products could be of interest in this region to quantify the soil to plant transfer coefficient. We acknowledge funding from the European Commission (AquaTRAIN MRTN-CT-2006-035420).

^{40}Ar /^{39}Ar thermochronology using plagioclase

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^{40}Ar/^{39}Ar thermochronometry using plagioclase holds tremendous potential for quantifying thermal evolution on Earth and other planetary bodies. Detailed diffusion experiments on single crystals of plagioclase from a gabbro in the Bushveld Complex yield activation energies of 36-48 kcal/mol, positively correlated with $\ln(D_0/a^2)$, which varies between 5 and 10, corresponding to closure temperatures of 200 to 300°C for a 10°C/Ma cooling rate. Age spectra generally conform to single-domain diffusive loss profiles, which suggests that grain-scale diffusion dominates argon transport in this homogenous plagioclase. The observed diffusion kinetics predict the differences in discordance observed in the age spectra (i.e. the most retentive grains have the least disturbed age spectra) and yield an internally consistent thermal history.

The cause of observed differences in diffusion kinetics between the plagioclase grains is not clear, but the differences appear to be inherent to each grain. ^{39}Ar and ^{37}Ar diffusion experiments on a variety of plagioclase with differing compositions and microstructural characteristics reveal an even larger range of apparent E_a and D_0/a^2 than that observed in the Bushveld gabbro. It appears that natural variations in plagioclase argon diffusion kinetics preclude a generically applicable set of diffusion parameters unless large uncertainties (± 100°C) are ascribed to them. However, when argon diffusion kinetics are quantified for each grain of interest, a sensitive thermochronology below 400°C can be attained.

Complexities arise in samples having microscopic exsolution. Arrhenius arrays are consistent with multiple diffusion domains or experimental coarsening of subgrain diffusion domains. Substantial Ca and K zoning also produces irregular Arrhenius plots, although corrections can readily be made if zoning is well characterized. Temperature cycling to lower temperatures often yields irreproducible results if measurements follow heating to ~800-850°C, possibly due a structural transition occurring during prolonged heating. More obvious deviations from linear Arrhenius arrays occur above ~950-1000°C. Taken together, this suggests much previous data acquired under suboptimal laboratory conditions and with multiple grains has questionable reliability.