

K-feldspar geochronology: Not just ³⁹Ar

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Bell-shaped Pb diffusion profiles are not found in U-Pb mineral chronometers; instead, patchy intra-grain age variations match heterochemical recrystallization [1]. Fluids most efficiently control micro-chemistry, micro-textures and the isotope record [2-5]. Is K-Ar different from U-Pb?

Some authors [6] propose that K-feldspar (Kfs) loses Ar in nature and the laboratory by the same mechanism, volume diffusion out of discrete "domains", so that a lab experiment can be inverted to yield a thermal history; they assume that ambient temperature alone uniquely controls Kfs ages.

We re-sampled and re-investigated the archetypal Kfs MH-10 [6]. We duplicated age spectra and Arrhenius trajectories of [6]; this is where agreement ends. The self-similarity of Arrhenian non-linearities demonstrates that "small domains", which were argued to be mathematically justified [6] even if physically untenable [7], are untenable mathematically as well. We characterized the sample by cathodoluminescence and electron microprobe, discovering at least 5 fluid-produced, heterochemical, diachronic mineral generations. This confirms [8]. Each diachronic Kfs generation has a different Ca/Cl/K signature. This confirms [9]. MH-10 records a geohydrothermal history of fluid interactions; its laboratory staircase spectrum is an effect of degassing a mixture of unrelated Kfs generations. This forbids reconstructing its "thermal history". In the own words of [6], the insight gained from MH-10 must be extrapolated to all existing Kfs samples. Thus, no Kfs must be used as a "thermochronometer" unless it were to be proven to be unaffected by patchy recrystallization and to have an isochemical Ca/Cl/K signature. What Kfs is suitable for instead is a detailed reconstruction of the hydrochronology of a rock.

[1] Williams et al, *Ann Rev EPS* **35** (2007) 137 [2] Cole et al, *GCA* **47** (1983) 1681 [3] Lasaga, *Miner Mag* **50** (1986) 359 [4] Putnis, in: Harlov & Austrheim, *Metasomatism and the Chemical Transformation of Rock*, Springer (2013) [5] Villa & Williams, in: Harlov & Austrheim, *Metasomatism and the Chemical Transformation of Rock*, Springer (2013) [6] Lovera et al, *Contrib Mineral Petrol* **113** (1993) 381 [7] Villa, *GCA* **61** (1997) **689** [8] Villa & Hanchar, *GCA* **101** (2013) 24 [9] Villa, *Geol Soc London Spec Pub* **378** (2013)

Coupling HTO tracer experiments and tomography imaging to monitor the effects of celestite porosity clogging on diffusion properties in porous media

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The focus of the present study is to characterize the effects of porosity clogging on the effective diffusivity of porous materials under geochemical perturbation. A systematic experimental approach was used, and coupled to pore network and reactive transport modeling.

The experiments were performed in diffusion cells composed of a column filled with synthetic silica spheres (SiLi beads) or purified sea sand and two reservoirs, containing a SrCl₂ and a Na₂SO₄ solutions. Prior to the mineral precipitation experiments the transport properties were characterized by means of conservative radiotracer (HTO) tests and revealed D_e values of (4.79 ± 0.24) × 10⁻¹⁰ m² s⁻¹ and (4.20 ± 0.21) × 10⁻¹⁰ m² s⁻¹ for SiLi beads and sea sand, respectively. The precipitation of celestite (SrSO₄) in the porosity and the subsequent evolution of the diffusivity were monitored by HTO and computed tomography (CT).

The CT resolution varied from 11 to 15 μm. The data were implemented into a pore network model (GEODICT) in order to estimate porosity and diffusivity of the materials, but also to monitor the precipitation processes in a non destructive way. The model was calibrated on a diffusion cell filled with SiLi beads of 400-600 μm particle size. The segmented CT porosity of 0.365 was comparable to 0.361 ± 0.047 for HTO radiotracer tests, giving confidence in the approach used. In addition, the porosity was cross-checked by mercury intrusion porosimetry measurements, which gave values of 0.389 and 0.413, in good agreement with the two precedent ones. In addition to the pore network modeling, a reactive transport model was developed to reproduce the data using Archie's law, in order to extend its applicability to very small effective porosities.