The multiple timescales of the hydrated proton

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Proton mobility in water involves low barrier hydrogen-bond (HB) reorganization, and is thus a succession of events occurring on a hierarchy of timescales. We have used Multi-State Empirical Valence Bond (MS-EVB3) simulations to investigate the mechanism of proton mobility in water [1]. On a short (fs) time-scale, we identify an asymmetric 'Eigen' cation, $H_3O^+(H_2O)_3$, which is dynamically distorted. It undergoes a 'special-pair dance' governed by cleavage of a 2nd-shell HB. After several special-pair exchanges, 'the' partner is selected and their O–O separation shrinks to that of the 'Zundel' cation, $H_5O_2^+(H_2O)_4$, which is shown to be a transition structure for proton hopping in water. The transfer within it is successful (not immediately reversing to the starting configuration) when the surrounding water environment is receptive to the new location of the charge. Approximately two solvation shells (about 20 water molecules) participate in product stabilization [2]. On longer timescales we observe diffusive kinetics, manifested by a pair correlation function exhibiting a power-law behaviour at long times [3].

[1] Markovitch *et al.* (2008) *J. Phys. Chem. B.* **112**, 9456–9466. [2] Lapid *et al.* (2005) *J. Chem. Phys.* **122**, 014506. [3] Chen *et al.* (2010) *J. Phys. Chem. B* **114**, 333–339.

Mantle wedge and slab fluids in Eastern Mediterranean arc magmas

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In the Eastern Mediterranean region a large volcanic belt developed over a wide area. These products are widespread from Macedonia to Rhodopes and Thrace, the North-Central Aegean and Western Anatolia, and range in age from Upper Eocene to Pleistocene. They are mainly high-K calc-alkaline and shoshonitic lavas, plus some scattered ultra-K lavas and dykes, high-Mg andesites and dacites. All these rocks share some geochemical features features, like LILE enrichments and Sr-Nd-Pb isotopic compositions, pointing out a common, mantle wedge source modified by subduction related metasomatism (e.g. Rb/Nb ≈ 9.1±3.8, Pb/Ce ≈ 0.38±0.17, $^{87}Sr/^{86}Sr \approx 0.7084\pm11$, $^{143}Nd/^{144}Nd \approx 0.51237\pm12$, on average over 1031 samples). In contrast, the South Aegean active arc are mainly tholeiitic to calc-alkaline in character, they have Fluid Mobile Elements to Fluid Immobile Elements ratios quite similar to rocks found north of the Pelagonian-Actic-Cycladic-Menderes massifs but are characterized by distinctly lower Sr and higher Nd isotopic compositions (Rb/Nb ≈ 5.6±3.5, Pb/Ce ≈ 0.19±0.06, $^{87}Sr/^{86}Sr \approx 0.7047\pm6$, $^{143}Nd/^{144}Nd \approx 0.51273\pm10$, on average over 695 samples).

These differences are attributed to two different pre-subduction mantle domains under the region: a lithospheric mantle wedge in the North and Central Aegean, and a depleted asthenospheric mantle wedge farther south, in correspondence of the South Aegean arc. These mantle wedges were metasomatized by slab-derived fluids, with almost the same nature and chemical composition. Indeed the continuous subduction of the Neotethys since at least the last 60-50 Ma, the volcanism of the two zones should be related to the same segment of the subducting plate, without slab ruptures and subduction jumps. The fluids released by the subducted Ionian lithosphere derive by metamorphic dehydration reactions occurred at the same, or close, P-T conditions, given the occurrence of a long lasting subduction of a slow, low-dipping slab.