The pH of the Dead Sea brine: Calibrating the combination electrode measurements

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While the pH is a major variable controlling the carbonate system speciation and the saturation state of carbonate minerals in aqueous systems, it's measurement in hypersaline brines is not trivial. In such media, a problem with liquid junction potential may arise when employing standard pH measurements using a combination pH glass electrode.

The hypersaline Dead Sea and its predecessor, Late Pleistocene Lake Lisan, precipitated sequences of seasonal aragonite laminae during most of their geological history. The seasonality in aragonite deposition from the Ca-chloride brines was attributed to supersaturation induced by mixing of the inflowing high bicarbonate fresh runoff water in the Ca-rich lake brine [1]. This study evaluates and verifies the pH measurements in Dead Sea brine and its mixtures with deionized water using a liquid-junction-free cell [2], consisting of a pH glass electrode (Orion 81-01) and Cl^- ion selective electrode, ISE (Orion 9417).

The voltage of the ISEs cell is proportional to the log activities product of H^+ and Cl^-. A calibration curve was prepared by measuring the ISEs cell voltage per incremental addition of 32% HCl to the brine. Cl^- activity was calculated based on the Pitzer data base and MacInnes convention using the PHREEQc software [3]. The pH values of the unknown brines were derived from the calibration curve by measuring the cell voltage and its major ion composition.

Simultaneous pH measurements by the ISEs and a standard combination pH glass electrode (Orion 81-03, calibrated with low ionic strength buffers) were conducted for comparison. It was found that the pH difference between the measurements by the two electrode system was linearly correlated with ionic strength. Hence, by applying appropriate correction factor it is possible to use a standard combination pH electrode to measure pH of very high ionic strength solutions. The pH of the surface brine of the Dead Sea was determined to be 6.28.

[1] Barkan *et al*. (2001) *GCA* **65**, 355–368. [2] Knauss *et al*. 1990, *GCA* **54**, 1519-1523. [3] Parkhurst & Appelo (1999), *USGS WRI* Rep. 99-4259.

Syn-Variscan anorogenic volcanism in northern Gondwana: SIMS U-Pb ages and REE patterns of zircon from deep borehole in coastal Israel

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The Helez Deep 1A borehole (southern coastal Israel) penetrated a 200 m thick (5977-5767 m depth interval) felsic volcanic section, the Gevim quartz porphyry, overlying Precambrian basement rocks and overlain by Triassic shales. Previous Rb-Sr and K-Ar dating of these volcanics yielded Permian and Jurassic ages, respectively, considered as recording rifting-related magmatism in the Levant margins of the NeoTethys. We present SIMS U-Pb dating of zircons separated from rock-cuttings recovered from 4 different depths within the volcanic unit (~10 zircon grains each), which yield Early Carboniferous crystallization age for the Gevim quartz porphyry. Zircons of the two deeper samples yield calculated concordia ages of 353 ± 3 and 345 ± 2 Ma (2σ), whereas for the two shallower samples 350 ± 10 and 355 ± 15 Ma discordia intercept ages were calculated. While separated zircon is fresh and idiomorphic, feldspar and micas, the major Rb and K carriers in felsic igneous rocks, are heavily altered to clay. The Rb-Sr and K-Ar clocks were thus reset by hydrothermal alteration. This is the first discovery of Early Carboniferous volcanism in northern Africa and Arabia. It closely follows uplift and erosion of several regional ‘Geanticlines’ and coeval with steep crustal thermal gradients in the Levant. Zircon REE patterns measured by SIMS indicate within plate 'A-type' granite affinity. The geodynamic setting of volcanism is thus extensional rather than of Variscan compression, possibly related to rifting and detachment of Gondwanan terranes that were eventually incorporated to the Variscan orogeny.

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