

Determining the pre-eruptive magmatic conditions and sulfur release of the AD1280 Quilotoa eruption, Ecuador

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Pre-eruptive conditions in the magma storage zone prior to the AD1280 eruption of Quilotoa volcano in Ecuador have been constrained using geothermobarometry; values of 240 MPa average magma pressure and f_{O_2} NNO+1.63 were calculated; a relatively oxidized, shallow magma of 800°C.

Using FTIR and EMPA on glass melt inclusions in quartz phenocrysts, total water dissolved in the melt was determined to be ~6.65 wt% (X_{H_2O} 0.21), of which 5.05wt% exists as H_2O_m while 1.6wt% is OH. CO_2 in the melt is variable. The average, 141ppm, corresponds to X_{CO_2} $1.8e^{-4}CO_2$.

Using CO_2 - H_2O solubility models, a melt X_{H_2O} 0.2 was computed – equal to the value measured in the melt, indicating water saturation at the time of trapping.

A dominance of H_2O over CO_2 is revealed in the vapor phase: 0.98 and 0.02 respectively.

Melt sulfur concentrations are 47-92ppm. Petrologic methods, magma volume- SO_2 degassing correlations and ice core records were combined to estimate values of 969 Mt H_2O and 2.25 Mt SO_2 degassed from the melt during the eruption, from which ≤ 3.4 Mt H_2SO_4 could have been produced (assuming 100% SO_2 -to- H_2SO_4 conversion) and a total of 35-75Mt SO_2 (melt + excess S vapor phase), producing ~52-115 Mt H_2SO_4 .

Origin of dissolved solids in Marcellus shale produced water

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Hydraulic fracturing of black shales for natural gas production results in large volumes of flowback and produced water, which rapidly (within days to weeks) achieves high levels of total dissolved solids (TDS), sometimes $>2 \times 10^5$ ppm. This highly saline water continues to be produced, albeit at much diminished rates, over the lifetime of the well. This brine could originate from (1) interaction of injected water with salts in the formation, (2) extraction of brine trapped in pores within the shale and/or (3) formation water previously held in fractures, sandy lenses, or adjacent strata. To evaluate the origin of these dissolved solids, we carried out sequential leaching experiments on dry-drilled cuttings from the Middle Devonian Marcellus shale and adjacent units in Tioga County, New York, USA. The samples were treated with ultrapure water to dissolve soluble salts and sulfates, 1N ammonium acetate buffered to pH 8 to extract exchangeable cations, 8% acetic acid to dissolve carbonate minerals and 0.1N HCl to target other acid-soluble phases.

The water leachates had consistently higher Na/Cl and lower Ca/ SO_4 , Na/Ca and Sr/Ca ratios compared to produced water [1, 2]. Ba/Ca ratios were highly variable (as in the produced water) and $>90\%$ of the Ba extracted was in the ammonium acetate fraction, suggesting it is bound in exchangeable sites within the shale. $^{87}Sr/^{86}Sr$ ratios of water-soluble and exchangeable Sr range from 0.7093 to 0.7112, mostly within the range of $^{87}Sr/^{86}Sr$ values measured in produced waters [1], but well above Devonian seawater and well below bulk-shale values (>0.731). Based on the significant differences between the chemistry of the leachates and that of Marcellus produced waters, we suggest that most solutes in the latter are inherited from highly saline formation waters in fractures or adjacent strata. Long-term interaction of these waters with the shale imprinted similar Sr isotope ratios on the water-soluble and exchangeable portions.

[1] Chapman *et al.* (2012) *ES&T* **46**, 3545-3553. [2] Haluszczak *et al.* (2013) *AppGeochem* **28**, 55-61.