

Metasomatism and melting in subduction-related volcanics: U-Th-Pa constraints from Vesuvius

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We argue that the highly undersaturated, incompatible element enriched lavas of southern Italy reflect the influence of a metasomatic component from subducted carbonate-rich sediments. Vesuvius in particular, provides a natural laboratory to study this process, located on an active margin where abundant clay-carbonate rich lithologies are currently subducting. Here we present new trace element and U-Th-Pa isotope data on historic potassic to ultrapotassic Vesuvius samples in order to constrain melting and metasomatic processes responsible for such petrologically distinctive rocks.

The samples display ubiquitous ²³⁸U excess (up to 27%) at relatively constant (²³⁰Th/²³²Th). This combination of significant ²³⁸U excesses in enriched arc lavas is extremely unusual and we attribute this to the influence of carbonate component. In striking contrast to the ²³⁸U excess, our new (²³¹Pa/²³⁵U) are among the highest reported for arc rocks. This further emphasises the decoupled U-Th and U-Pa systems seen elsewhere in arc volcanics. We reproduced the observed U-Th-Pa data with a dynamic melting model modified with the assumption that the amount of added U-rich hydrous melts is reflected by an increase in degree of melting (and in melting rate). In this model, ²³¹Pa-excesses are generated by 'in-growth' but the ²³⁸U-²³⁰Th excesses still dominantly reflect addition of a subduction related component.

More generally we try to relate the case study of Vesuvius to the array of highly alkalic Italian magmatism. We suggest two distinct episodes of melting and metasomatism occurring at different depths and timescales in the down-going slab beneath Vesuvius. Firstly, an episode of sediment melting below the solidus of carbonate phases at shallow depths which can generally explain the K-rich magmatism of the Italian volcanoes. Secondly, a recent episode of U-rich hydrous melts from carbonate- and clay-rich subducted metasediments, generated at the current depth of the slab beneath Vesuvius (>350km), can explain the observed ²³⁸U excesses.

Pyrite oxidation at seafloor conditions: Inorganic mechanisms

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Sulfide oxidation and weathering are important processes that govern the global iron and sulfur cycles both in terrestrial habitats, where sulfide oxidation gives rise to acid rock drainage (ARD), and at deep sea hydrothermal vents, where sulfide oxidation provides the necessary energy source to a large variety of biological processes. There have been many studies investigating the ARD related inorganic and biogenic mechanisms of sulfide oxidation and recently some studies also followed pyrite oxidation processes in deep sea environments. However, experimental studies of pyrite oxidation typically used changes in bulk solution chemistry normalized to the surface area of pyrite in equilibrium with the solution to evaluate the reaction kinetics and mechanisms. Yet the changes at the surface of the pyrite grains have so far been difficult to evaluate. We will present here for the first time rate and mechanism data for the inorganic oxidation of pyrite in synthetic hydrothermal vent fluid and in seawater from experiments that combined the bulk changes in solution chemistry with a quantitative 3D volume loss evaluation via vertical scanning interferometry (VSI). With this approach we could directly determine the mass of pyrite lost over the course of the reactions (mol/cm²/min).

Single pyrite grains (~1mm²) were reacted for 1 to 12 weeks with a synthetic hydrothermal vent fluid or a seawater solution, both under anaerobic conditions at ~25°C under gently stirred, dark conditions. The bulk chemical changes in the solution composition (e.g., SO₄, Fe²⁺/Fe³⁺) were evaluated using ion chromatography and spectrophotometric techniques, while volume loss was measured directly using VSI. For each pyrite grain, 3D surface topographic maps were obtained prior and after each time step, with a 1/3 or the pyrite grain being masked prior to the experiment in order to obtain a reference surface. After the experiment, the mask was removed and a second VSI scan obtained, which was subtracted from the original VSI scan of the unreacted pyrite surface. Using a specially developed Matlab code, the 3D volume loss during the reaction could be calculated from this direct measurement and this could be used to derive rates.

Preliminary VSI results yielded rates of 3x 10⁻¹⁵ mol/cm²/min in the vent fluid and 6x 10⁻¹⁶ mol/cm²/min in the seawater experiments. This data will be discussed and compared with previous literature data of bulk dissolution/oxidation of pyrite.