

The role of crustal assimilation on the oxidation state of arc magmas

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Oxygen fugacity (fO_2) governs magmatic evolution, phase assemblage, and gas speciation. Magmas erupted in volcanic arcs tend to be several orders of magnitude more oxidized than those at mid-ocean ridges, however the processes that lead to oxidation have not been identified. Here, we explore two mechanisms that may influence the fO_2 recorded by subduction-related volcanic rocks: 1) post- or syn-eruptive alteration, and 2) assimilation of continental crust. We use several proxies to estimate the fO_2 recorded by lavas, pumice and scoria erupted from the Central Volcanic Zone of the Andes: 1) whole rock $Fe^{3+}/\Sigma Fe$ ratios, 2) $Fe^{3+}/\Sigma Fe$ ratios in quartz- and olivine-hosted melt inclusions using micro X-ray absorption near-edge structure (XANES) spectroscopy, and 3) magnetite-ilmenite oxybarometry. Samples span a range of crustal contribution, as indicated by their radiogenic isotope compositions ($^{87}Sr/^{86}Sr = 0.705-0.712$), and cover the full suite of magma compositions erupted during the Neogene history of the arc (52 - 74 wt.% SiO_2). $Fe^{3+}/\Sigma Fe$ ratios range from 20-80% in these samples. This full range is observed for all stages of magmatic differentiation (basaltic andesites to rhyolites), all extents of crustal assimilation (30-100%), and all types of eruptive product (lavas, pumice and scoria). Comparison of the fO_2 calculated from bulk $Fe^{3+}/\Sigma Fe$ ratios (post-eruptive) versus that calculated from Fe-Ti oxides or melt inclusion $Fe^{3+}/\Sigma Fe$ ratios (pre-eruptive), enables us to quantify the effect of post- or syn-eruptive alteration. Some sample suites show excellent agreement between the three techniques employed in this study. In other cases, where pumices show evidence of alteration in hand-sample, the fO_2 recorded by bulk $Fe^{3+}/\Sigma Fe$ ratios is two orders of magnitude more oxidized than corresponding ratios from melt inclusions or oxybarometry, suggesting modification of whole rock $Fe^{3+}/\Sigma Fe$ ratios by post-eruptive processes. Our work demonstrates that care must be taken when exclusively relying on bulk techniques to determine magmatic fO_2 , as whole rock may be subjected to post-emplacement oxidation. Moreover, our results show that neither crustal assimilation nor crystal fractionation systematically oxidize bulk continental arc magmas.

Fluid-mineral interactions of CO_2/O_2 , NaCl-brines and siderite-ankerite-mixtures at geological CO_2 -storage conditions

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An option considered for the geological storage of CO_2 in Germany is the injection into deep saline aquifers. The geochemical effects triggered by impurities or so called incidental associated substances in CO_2 streams are an issue for mineral trapping of CO_2 . The carbonates siderite and ankerite are possible sequestration products of mineral trapping of CO_2 or can already initially occur in the target formations.

In the presented set of experiments the effect of O_2 in the CO_2 stream on siderite-ankerite-mixtures will be investigated. These experiments are conducted in static Au-Ti-cells at 20 MPa and 353 K with CO_2 containing 4 mol% O_2 . Saline groundwater is simulated by using a 2.7 mol/kgW NaCl-brine. Solution sampling during the the experiment is performed to monitor changes in the solution composition and thus mineral dissolution and precipitation reactions. First results of a reference experiment without the addition of O_2 (to be compared with the experiment containing O_2) show the expected dissolution of the siderite-ankerite-mixture (release of Ca, Mg, Fe and Mn). During the further course of the experiment a decrease of Fe- und Mn-concentrations indicates the formation of a new mineral phase, e.g. a Mn-rich siderite. Scanning-electron-microscopy (SEM) supported this assumption by revealing Fe- and Mn-rich precipitates on the mineral surfaces which were likely formed during the experiment. This and other assumptions will be further tested by deploying isotopically labeled CO_2 in upcoming experiments.