Dissolution rates of volcanic glasses of different chemical compositions

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Volcanic activity on land and on mid-ocean ridge systems produces huge amounts of volcanic glasses. Quenching of magma along oceanic ridges generate ca. a billion cubic meters (1 km^3) of glass each year (Morgan and Spera, 2001). Hence, the volcanic glass weathering and dissolution plays a pivotal role in the global cycling of a significant number of elements and of CO_2 (Staudigel et al. 1989, Brady & Gíslason, 1997). Although large explosive eruptions on land commonly produce volcanic glass (ash, tephra) of andesitic to rhyolitic composition, limited data are available on the short and long term dissolution rates of these glasses. This kind of explosive volcanic eruption, however, may affect significantly the composition of the ocean surface and of terrestrial surface waters (Frogner et al. 2001).

Towards the quantification of the role of volcanic glass in surfacial processes, tephra of various chemical compositions was sampled. The composition of the glasses ranges from 47 wt.% to 73 wt.% SiO_2 of both tholeiitic and transitional compositions. The ash samples were dried, ground with minimum strain to create fresh reaction surfaces, dry sieved to obtain the size fraction between 45 µm and 125 µm and ultimately cleaned ultrasonically with acetone. Resulting glass powders were dissolved in mixed flow reactors to determine their far from equilibrium steady state dissolution rates at 25°C and pH 4. Because our experimental results indicate that glass dissolution rates are proportional to geometric rather than BET derived surface areas, rates in this study are normalised to the former. The logarithms of measured geometric surface area normalised dissolution rates (mol/m^2/s) decrease monotonically from –8.8 for basaltic to –9.9 for rhyolitic glasses, spanning a range of one order of magnitude. The temperature effect on the dissolution rates yields apparent activation energies between 30 to 40 kJ/mol, irrespective of the chemical composition of the glasses.

References

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Arsenic association with iron sulphides, adsorption and incorporation

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The low-temperature association of arsenite and arsenate with disordered mackinawite, FeS, and pyrite, FeS_2, was studied experimentally. Disordered mackinawite forms in sulphidic environments as a metastable precursor to pyrite [e.g. 1], an important arsenic sink [2]. A better understanding of the association of arsenic with iron sulphides would help in unravelling an important part of the geochemical cycle of arsenic and in predicting the mobility of arsenic in sulphidic environments. Our work broadly followed two lines of approach.

Firstly, the adsorption of arsenite (As^{3+}) and arsenate (As^{5+}) onto disordered mackinawite was studied. Results show adsorption maxima at circumneutral pH and very fast (i.e. within a minute) adsorption kinetics for both As species. At increasing As concentrations, arsenite adsorption converted to coprecipitation while arsenate showed a Langmuir type adsorption. No unequivocal evidence for As^{5+} reduction by FeS was found in these experiments.

Secondly, the incorporation of arsenic into pyrite during the H_2S-oxidation pathway of pyrite formation [1] was examined. Results indicate that high arsenate concentrations (i.e. = 1mM) inhibit pyrite formation through the complete oxidation of the precursor FeS to elemental sulphur, while high arsenite concentrations inhibit pyrite formation probably through stabilisation of FeS. Lower arsenic concentrations do not influence the conversion of FeS to pyrite, nor the resulting pyrite habit. Arsenic is associated with the pyrite phase in the end product mixtures of pyrite and mackinawite.

Combining these results, several pathways of arsenic immobilisation in natural ambient temperature anoxic environments are revealed: (a) adsorption of low concentrations of arsenic onto the precursor FeS and incorporation in pyrite, leading to a relatively unreactive As sink; (b) adsorption of high concentrations of As onto the precursor FeS without subsequent conversion to pyrite, leading to an easily remobilised As sink; (c) adsorption onto an existing pyrite surface, leading to a relatively unreactive As sink.

References

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