American Mineralogist, Volume 107, pages 2153–2154, 2022

HIGHLIGHTS AND BREAKTHROUGHS

Oxidation of arcs and mantle wedges: It's not all about iron and water

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The geologic cycle and the role that plate margins play in the production and destruction of Earth's crust are key components to teaching some of the outcomes and implications of plate tectonics. Connections are woven, linking the distribution of magmatism around Earth and the distribution of plate margins, and relationships between the style and composition of magmatic products are explored. Students in the Earth Sciences are familiarized with the role of decompression partial melting at divergent plate margins and the crucial role of water in promoting the production of arc magmas in subduction zones by lowering solidus temperatures. With progression through an Earth Science curriculum, the role that water and volatiles exert over subduction and arc processes is expanded, and understanding their influence on the chemical and mechanical properties of subduction systems is deepened.

An important part of many igneous petrology courses is discussing the contrasting compositions, chemistries, and mineral assemblages between tholeiitic magmas, most commonly found at divergent plate margins, and the calc-alkaline magmas of volcanic arcs. Differences such as their divergent trends on AFM diagrams, the more common occurrence of hydrous minerals in arc systems, and the designation of arc magmas to be chemically more oxidized and oxidizing with higher oxygen fugacities are common. This chemistry-based characterization of arc magmas is commonly linked to processes in the sedimentary packages that sit on the subducting slab and under the mantle wedge. The loop is somewhat simplistically closed by attributing many of these mechanical, thermodynamic, chemical, and compositional traits in arc magmas to the release of water (and volatiles) from the sedimentary package, their role in partial melting, and the incorporation of volatiles into arc magmas.

However, the description of magma as oxidized, or oxidizing, should not be conflated with an abundance of water but as a matter of rock and magma oxidation state. A complementary perspective views the mineral assemblage, or oxidation state of species in magma, and considers their potential to accept or donate oxygen. The acceptance or donation of oxygen, from a chemistry perspective, is tied to the capacity of elements to donate or accept electrons through reactions that may be considered reducing or oxidizing and collectively describe the REDOX state of a system.

Many geologic systems, including progressively metamorphosed sedimentary packages in subduction zones and partial melts produced in arcs, have oxygen fugacities that are constrained by mineral assemblages that act as REDOX buffers. These systems are most strongly controlled by several relatively abundant elements in the Earth that may occur in more than one oxidation state. As the fourth most abundant element in crustal rocks, the iron (Fe) oxidation state is commonly cited as an element that is an important factor in the REDOX state of geologic systems. The availability of Fe and the ratio of Fe^{2+} to Fe^{3+} contribute to the thermodynamic stability of Fe-phases in igneous and metamorphic systems, and minerals that may accommodate both species are important monitors of oxygen fugacity. The $Fe^{3+}/\Sigma Fe$ ratios in magmas, rocks, and minerals may change, reflecting the availability of oxygen in a system. Zhang et al. (2022) describe the role of amphibole fractionation and how the accumulation of amphiboles, particularly in mature island arcs, influences bulk $Fe^{3+}/\Sigma Fe$ ratios and the REDOX state of the crust. This mineral-oriented approach linking mineral composition to the chemical state of systems in arc magmas leads to knowledge of the chemical status of arc crust. It has also been proposed that sulfur (S) and carbon (C), because of their relatively high abundances in pelagic sediments, may be important contributors to the oxidation state of the mantle wedge. However, several workers have observed that these elements may enter the subduction zone in a reduced state, and as such, are not capable of reacting to a more reduced state and releasing oxygen into the slab-derived fluids that contribute to the oxidation of the mantle wedge.

Song et al. (2022) leverage this mineral crystal-chemistry approach to establish another vector to the discussion on what causes increases in oxygen fugacity in the mantle wedge over a subduction zone with consequences for the composition and chemistry of arc magmas and resulting crust. Using examples of ferromanganese pelagic sediments metamorphosed to high-pressure conditions in the Qilian subduction complex, northwest China, Song et al. (2022) note that Fe^{3+} remains stable in assemblages that reached depths of >100 km and were partitioned into hematite, aegirine, and garnet. The stabilization of ferric Fe in high-pressure systems reduces the contribution that the reduction of Fe would make to increased oxygen fugacity. Meanwhile, the occurrence of hematite, in the absence of magnetite, suggests that the assemblages must have, simultaneously, been formed at conditions characterized by extremely high oxygen fugacity and well above the hematite-magnetite (HM) buffer. These twin observations raise the question of what other sources of oxygen are available in subduction zones.

The high-pressure metamorphic siliceous rocks described by Song et al. (2022) are intercalated with lawsonite-bearing eclogites, blueschists, and serpentinites from the North Qaidam ultrahigh-pressure metamorphic belt. The high-pressure rocks are characterized by Mn-(Fe)-rich assemblages that include quartzite-rich schists, Mn-Fe nodule-bearing quartzites, and aegirine-hematite-pyrxomangite quartizes, which are produced

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0003-004X/22/0012–2153$05.00/DOI: https://doi.org/10.2138/am-2022-8802

by the metamorphism of protoliths that may be described as pelagic sediments from deep ocean basins.

In the Qiliam locality, progressive metamorphism produced high-pressure assemblages that contain pyroxmangite ($Mn^{2+}SiO_3$), the Mn-members of the epidote group piedmontite $\{[Ca_2][Al_2Mn^{3+}](Si_2O_7)(SiO_4)O(OH)\}$ and sursassite $[Mn_2^{2+}Al_3Al_3(SiO_4)(Si_2O_7)(OH)_3]$, and ardennite $[AsMn_4^{2+}Al_4(AlMg)(AsO_4)(SiO_4)_2(Si_3O_{10})(OH)_6]$, another rare Mn-sorosilicate mineral. Song et al. (2022) describe and quantify the chemical speciation of Mn and its progression through the life cycle of pelagic sediments, noting that the majority of Mn is deposited in the 4+ state in phases that include Mn-(Fe-Ti)-oxide phases and Mn-rich clays.

The high-pressure Mn-silicate assemblages are all characterized by Mn in a more reduced state than occurs in the typical assemblages of pelagic sediments. Consequently, the progressive metamorphic reactions that produced these minerals simultaneously released oxygen into the system. The authors propose that this oxygen becomes chemically available to modify the oxygen fugacity of the mantle wedge and partial melts being produced that contribute to arc magmas and the formation of arc crust.

Manganese is the tenth most abundant element in Earth's crust, and its abundance and behavior in sedimentary systems are of interest to a diversity of researchers, ranging from those who propose sediments and ferromanganese crusts as a storehouse of critical metals (Lusty et al. 2018), to those studying factors impacting REDOX conditions in sediments and implications black shales (Calvert and Pedersen 1996) and preservation of hydrocarbon resources (Abubakar et al. 2022); REDOX conditions also modify the bioavailability and transport of contaminants (Borch et al. 2010), so improved knowledge of the behavior and participation of REDOX sensitive elements, including Mn, is an important part of understanding Earth's geochemical cycles. Meanwhile, subduction zones, forearcs, and volcanic arcs are important contributors to the planetary-scale flux of volatiles. Based on currently understood rates of subduction and global estimates for the abundance of MnO in sediments entering subduction zones, Song et al. (2022) propose that progressive reduction of Mn may release as much as $\sim 1.27–1.28 \times 10^{12}$ g/year oxygen. An implication of ferric iron (Fe^{3+}) being transported to greater depths in subduction zones is its transportation into the mantle, where it may play a smaller, perhaps minimal role in changing the oxidation state of sub-arc mantle and arc magmas, particularly when subducted peglagic sediments are Mn-rich. The contribution provides a thought-provoking point of discussion for upper division petrology courses, integrating petrography, crystal chemistry, and geochemistry in ways that simultaneously expand upon and challenge presumptions and assumptions about large-scale Earth processes.

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MANUSCRIPT RECEIVED SEPTEMBER 22, 2022
MANUSCRIPT ACCEPTED SEPTEMBER 22, 2022
MANUSCRIPT HANDLED BY HONGWU XU