Chapter I:

Introduction

(PART I)

Observations associated with convergent margins, including analyses of lavas and xenoliths collected at the surface, seismic imaging, and measurements of dynamic topography and gravity and geoid anomalies can be used to remotely detect properties of the mantle wedge and to interpret processes operating within that important region. The story is a complicated one, including fluxing of the mantle by slab-derived components, origins of initial and progressive mantle depletion, a complex pressure and temperature structure, and considerations of melt and fluid migration within the solid flow field. Nevertheless, understanding of first-order processes occurring within the mantle wedge can lead to larger-scale implications including the transport of fluid-modified slab-adjacent material into the deep mantle [1-6], origins of the continental crust [7, 8], time-dependent changes in slab dip angle [9], and controls on back-arc volcanism [10].

There is general agreement that fluids from a dehydrating slab are introduced to the wedge as the slab descends and that the pressure-temperature path, chemical composition, and phase equilibria within the slab determine the locations of water-rich fluid release [2]. The delivery of this water-rich fluid phase into and interaction with the overlying mantle induces hydration reactions within the peridotite and, where temperature is sufficient, water-fluxed melting [11]. Major element abundances in arc lavas are derived from partial melting of the wedge peridotite above the slab, but large-ion lithophile elements (LILE) and other incompatible elements can be traced to slab-derived influences such as sediment melting [12, 13], dehydration of the altered oceanic crust [14], or dehydration of subducting serpentinized lithosphere [2, 15]. In general, convergent margins involve lavas that are enriched in incompatible fluid-mobile elements and depleted in incompatible high field strength elements [16-18; others], suggesting a significant connection between fluid introduction and melt production.

A particular part of the subduction system where strong coupling between mass and energy flows and geophysical and geochemical processes is most important is the mantle wedge immediately adjacent to the slab. Conventional steady-state thermal solutions of subduction indicate that the slab-wedge interface is too cold for even water-saturated melting of peridotite, so the fluids must somehow migrate into hotter areas of the wedge in order for melting to begin [19]. Migration and equilibration of fluids with peridotite can lead to higher concentrations of water in nominally anhydrous minerals (NAM) and to the stabilization of hydrous phases. The effect of increasing water content in NAM is twofold: (i) decreasing solidus temperatures [20, 21] and (ii) water-weakening that reduces the viscosity of the solid material [22]. As such, there is a dual effect of hydrous fluid introduction on the geochemistry of initial melts within the system and on the force balance within the wedge.

The depth interval and the magnitude of fluid release from the subducting plate are a function of parameters such as slab age and convergence velocity as well as the composition of the descending plate [23]. Specifically, the different lithological fluid sources emphasized by different subduction parameters allow for changing fluid addition patterns (mass and fluid-mobile trace element chemistry) along the length of the subducting plate through the upper mantle [23, 24]. These patterns may directly influence the composition and mass fraction of fluxed melts within the wedge, leading to regional variations in arc lava geochemistry. Variations can be compared among different subduction systems, or through cross-arc and along-arc trends within the same subduction system. For example, relative contributions from heterogeneous slab fluid sources can be manifested in diverse chemical characteristics of lavas derived from different depths above the seismic Wadati-Benioff zone (WBZ) [18, 25, 26].

Subduction zones can be generally described as having topographically depressed back-arc regions and overlying plates, long-wavelength geoid highs over slabs, and shorter wavelength geoid lows over trenches [27, 28]. Long-wavelength geoid highs are interpreted as indicative of a radial viscosity structure leading to regional compensation of subducting slabs [29, 30]. However, shorter-wavelength geoid anomalies and the depth of back-arc basins may be resolved by studying viscosity variations caused by thermal or compositional factors within the upper mantle [28]. Along the slab-mantle interface, the viscosity structure is strongly dependent on both temperature and composition (water-weakening) [22]. A localized low-viscosity region in the mantle wedge has been shown to have a substantial effect on the force balance in a subduction zone, and leads to observable signals in topography, state of stress, gravity, and the geoid [28, 31-33]. While the importance of such a region in a subduction zone has been evaluated, the mechanism by which it develops and its detailed geometry have yet to be completely investigated.

Modeling that addresses principally either the force balance or the chemistry, using results from one area to infer behaviors in the other, has succeeded in reaching broad conclusions as to the manner of hydration of the mantle wedge and melting beneath the arc [24, 34-39]. However, when the thermal structure, viscosity, and the solid flow field are addressed within the context of a fully coupled geophysical and geochemical model, emphasizing the importance of interdependent contributions, more detailed interpretations can be made. Therefore, understanding of subduction zones requires a model that accounts for complex interactions between chemical and dynamic features of the system. The evolution of dynamical quantities such as the flow field, entropy, and bulk composition should provide input to thermodynamic calculations, which output chemically-governed quantities such as melt fraction, compositional buoyancy, water speciation, and latent heat contributions to the thermal balance. This forms an essential loop where neither chemistry nor physics are independently evaluated. Indeed, it is the dependence of one on the other that presents insights into the subduction system on a fundamental level. This thesis investigates subduction processes from fluid release to melting within a coupled, internally consistent geochemical and geophysical modeling treatment, emphasizing the origination, development, and implications of hydration features within the wedge as a function of regional subduction parameters.

Chapter 2 is a presentation of GyPSM-S (**G**eod**y**namic and **P**etrological **S**ynthesis **M**odel for **S**ubduction), a self-consistent model that includes the thermodynamic minimization algorithm pHMELTS [20, 40, 41], which takes into account water partitioning into NAM, in conjunction with the 2-D thermal and variable viscosity flow model ConMan [42] and a fluid migration scheme. Evaluation of properties such as the melt fraction, fluid flux, the impact of water in NAM on the viscosity structure and overall flow field, and spatial extent of fluids and melts within the subduction system are all incorporated into GyPSM-S. The significance of the coupled scheme is the detailed tracking of fluids and their rheological and chemical effects from release to initiation of melting. The primary results of the GyPSM-S models confirm the conclusions of earlier models of spatial separation between the slab interface and the regions of melt initiation in addition to introducing the existence of a low-viscosity channel (LVC) within the mantle wedge, the process by which LVCs form, and the limitations on LVC geometry. The low-viscosity region is shown to be a robust feature that is stable over a range of subduction parameters.

In order to demonstrate the applicability of GyPSM-S results to geochemical datasets, a supplemental modeling approach is required to account for the addition of fluid-mobile tracers and to make detailed inferences as to the geochemistry of arc lavas with respect to slab fluid sources and as a function of changing subduction parameters. Chapter 3 presents an extension of the results of GyPSM-S to specific mass tracing. A source-based approach is employed to determine how slab dehydration changes with changing subduction model parameters and how this influences the major and trace element chemistry of fluid-fluxed melts within the wedge. Consequences of different degrees of interaction between fluids and hydrated peridotite within the LVC are investigated, and cross-arc and along-arc variations in regional geochemical datasets are compared to the model results with an emphasis on changing slab fluid-source lithology. Additionally, there is discussion of simple melt migration scenarios which may preserve relative heterogeneities in melts initiated at different locations within the wedge. Interpretations of the results lead to several potential mechanisms to produce hydrous inputs to back-arc source regions.

The influence of the existence of the LVC, and other localized low-viscosity geometries within the wedge, on the overall flow field and force balance can be evaluated by surface observables particular to the viscosity structure, such as the topography and gravity and geoid anomalies [31, 32]. While it is well understood that localized low-viscosity regions may be important to the force balance within mantle wedges, the mechanisms of development of these regions and how the regional geometries change based on changing subduction behaviors have been established only recently (Chapter 2). The logical next step would be to attempt to match observed geophysical signals in a particular locality with a modeled fluid-source-based hydration structure. Chapter 4 presents the impact of GyPSM-S modeled localized low-viscosity regions on the topography and geoid and gravity anomalies for the northern Izu-Bonin subduction system, particularly emphasizing the manner of development of the low-viscosity region as the primary influence on the geometry and comparing model results with observed signals.

(PART II)

A greenish coloration in synthetic quartz can arise from irradiation of quartz, heating of quartz originally of another color, or from the presence of ferrous iron within the structure [43-46]. Upon irradiation, an electron will migrate away, leaving a "hole center," and the associated charge-compensating cation will migrate away through the structure as well [47]. Heating of quartz can thermally activate color centers and encourage migration of species within the structure. By destroying color centers, heat treatment can selectively eliminate components of coloration associated with exposure to ionizing radiation. The presence of molecular H_2O within the quartz structure has been found to be detrimental to the development of certain colors and may allow other colors to emerge instead [48]. However, natural examples of greenish coloration in quartz are rare [49-51], and have not been fully discussed within the context of their environment of formation or in relation to other associated colors of quartz. Both amethyst and smoky quartz have been found to be closely associated with natural examples of greenish quartz. The violet coloration in amethyst is due to the removal of an electron by high-energy radiation that results in oxidation of ferric iron within the quartz structure to Fe^{4+} [52]. Commonly characterized by a brownish gray hue, smoky quartz represents another color variety of quartz produced by ionizing radiation. The smoky color center is modeled as Al^{3+} substituting into the Si^{4+} tetrahedral site, with associated charge-balance fulfilled by a nearby positively charged ion (such as Li^{+}) in an interstitial site.

The Thunder Bay Amethyst Mine Panorama (TBAMP) deposit is the site of an extinct hydrothermal system that flowed through a fault and led to mineralization primarily by quartz [53]. Although most of the quartz is amethystine, natural greenish quartz has been found in the TBAMP in several distinct varieties. Yellowish green quartz and dark green quartz with purple hues are found as loose detritus within the TBAMP (originating from outcroppings), and pale greenish gray quartz is found as part of an outcropping color-gradational sequence involving macrocrystalline quartz of other colors, including colorless and smoky gray, and chalcedony. The color-gradational sequence occurs solely in a localized zone, which may be the site of initial influx of fluids into the fault. Distally, the color of the *in situ* quartz is dominantly dark violet amethyst. In some cases, this dark violet amethyst, when cut perpendicular to its *c* axis, is found to be composed of alternating sectors of colorless and dark purple quartz. McArthur et al. [53] proposed that greenish coloration at TBAMP was heat-induced “bleaching” of amethyst.

Chapter 5 presents a study involving visual observations and spectroscopic analyses of the different color varieties in the TBAMP system interpreted specifically in association with radiation exposure and heat-treatment experiments. It is important to understand the origin of the greenish color because it is ubiquitously present within a progressive color sequence in quartz. Clues in the chemical and spectroscopic variations within the sequence may provide an increased understanding of the development and persistence of radiation-induced color centers in quartz within the context of changing chemical, thermal, and kinetic factors in a hydrothermal system.

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