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The Earth as a multiscale quantum-mechanical system

Pascal Richet [a,*], Giulio Ottonello [b]

[a] Institut de physique du globe de Paris, 1, rue Jussieu, 75005 Paris, France
[b] DISTAV, Università di Genova, Corso Europa 26, 16132 Genova, Italy

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ABSTRACT

Major features of the Earth's structure and dynamics originate in the contrast between the rigidity of Si–O bonds and the softness of Si–O–Si linkages. Because this contrast results from orbital hybridization, a real understanding of bonding relies on *ab initio* quantum-mechanical principles. As investigated with first-principles interatomic potentials, the α–β transitions of SiO_2 polymorphs illustrate how soft Si–O–Si linkages give rise to dynamical structures at rather low temperatures and yield the low melting temperatures of SiO_2-rich minerals that are at the roots of SiO_2 enrichment in magmatic differentiation. The increasing concentration of alkalis throughout this process is another aspect that must also be studied in terms of molecular orbitals in relation with the presence of aluminum in tetrahedral coordination. Finally, calculations of noble gas solubility show that some important features can be treated with "hybrid" calculations when, in addition to quantum-mechanical effects, the energy needed to create a cavity in the silicate melt is dealt with in a classical manner.

1. Introduction

Ever since the earliest phases of the history of our planet, the main physical and chemical features of the Earth have been determined by magma differentiation. Continent growth has for instance been the ultimate result of fractional crystallization whereby basaltic magma, formed by partial melting of mafic rocks at depth, progressively gives rise to rhyolitic or phonolitic melts through precipitation and settling of SiO_2-poor ferromagnesian minerals not far from the Earth's surface. Depending on the initial composition of magma, the petrogenetic series that have been distinguished are characterized by different evolutions (Fig. 1), but they share the common feature of marked relative increases in the contents of SiO_2, Al_2O_3 and, especially, of alkali oxides. Correlatively, strong decreases in the contents of alkaline earth oxides take place. These systematic changes in chemical composition induced by fractional crystallization are associated with important variations of physical properties, which have themselves far-reaching consequences for magma transfer and geodynamic processes. To give a single example, continents are less dense than the mantle so that they escape subduction cycles and remain distinct from the upper mantle simply because of the impossibility to pack compactly SiO_4 and AlO_4 tetrahedra in the three-dimensional networks of quartz and feldspars, the two main constituents of granite.

Curiously, however, the fundamental principles governing magma differentiation have received little attention, even though Osborn (1950) long ago pointed out the relevance of ion properties such as field strength and electronic configuration. Actually many basic features of silicates such as the four-fold coordination of Si^{4+} cations by oxygen anions can be accounted for in terms of ionic forces (cf. Mysen and Richet, 2005). But it is generally

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* Corresponding author.
E-mail address: richet@ipgp.fr (P. Richet).

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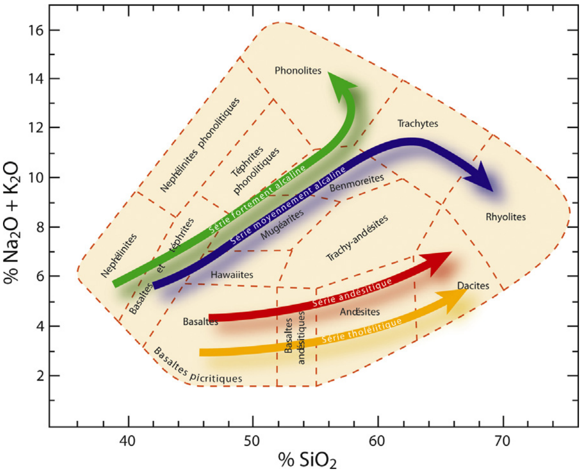

Fig. 1. (Color online.) The main petrogenetic series, beginning with the various types of basalt magma and ending with phonolites, rhyolites and dacites, as indicated by the variations of SiO_2 and alkali oxide contents. Cox et al., 1979.

incorrect to assume complete electron transfer between the oxygen and the metals with which they bond and, thus, to approximate anions and cations as closed shells interacting through Coulombic forces and short-range repulsion. In other words, fundamental issues in Earth sciences cannot be addressed in terms of atomic bonding with the assumption that bonding lacks directionality and depends only on nominal ionic charges and interatomic distances.

Hence, the question that remains to be investigated is how the structure and dynamics at all length scales within the Earth are determined at a microscopic scale by interatomic potentials and chemical bonds and, thus, by electronic distributions between bonded atoms. As stated in these terms, major questions of geochemical and geophysical interest can be answered only within the framework of quantum mechanics. Even though various kinds of first-principles calculations are now routinely performed not only for minerals, but also for melts (*e.g.*, Ispas et al., 2001), they have generally focused on specific problems in mineral physics without specifically addressing their broad geochemical or geophysical consequences.

In this paper, our goal is to substantiate our claim that, despite its immense size, the Earth as we know it has to be studied from a quantum-mechanical perspective. It would be far beyond our scope to review even briefly the quantum-mechanical methods currently used to investigate bonding in condensed phases (*e.g.*, Gatti, 2005). Rather we will discuss in general terms four different topics. We will first examine the α–β transitions of tectosilicates to show that the anomalously low melting temperature of SiO_2, which is at the very roots of magma differentiation, is a direct consequence of soft Si–O–Si linkages. We will then examine this directionality in terms of orbital hybridization in pure SiO_2 before turning to a closely related question, namely, the manner in which AlO_4 tetrahedra are stabilized within the silicate networks of SiO_4 tetrahedra thanks to electron transfer from charge-compensating cations. We will finally consider the supposedly inert noble gases, whose relative abundances carry important information on the Earth's early history (*e.g.*, Ozima and Pososek, 2001), to discuss how their solubility in silicate melts is determined by the creation of cavities large enough to host them. Basic quantum-mechanical concepts and common acronyms have to be used to deal with these issues. Rather than introducing them anew, we prefer to refer to Tossel and Vaughan (1992) for an introduction to the realm of "Quantum Geochemistry".

2. α–β transitions and melting of tectosilicates

The considerable SiO_2 enrichment that is the predominant feature of magma differentiation is in fact paradoxical. The first crystals to precipitate in a multicomponent system are the most refractory, *i.e.*, they have the highest melting points. In accordance with Lindemann's (1910) early ideas, they are assumed to have the strongest interatomic bonds because melting is usually associated with bond breaking caused by mean square vibrational amplitudes exceeding some critical fraction of bond distances. Now, Si–O bonds are commonly supposed to be the strongest in silicate systems because of the small radius (r) and high nominal electrical charge (z) of the Si^{4+} ion compared to those of other major cation-building minerals (Fig. 2). On the basis of ionic forces, one would expect SiO_2 to melt at a much higher temperature than CaO and MgO, but the reverse holds true. Whereas the melting temperature of cristobalite, the high-temperature polymorph of SiO_2 is 1999 K, CaO and MgO melt at temperatures higher than 3000 K. As a consequence, one would expect the silica content to decrease progressively upon fractional crystallization, which clearly contradicts the evolutions that take place along the petrogenetic series.

To account for this anomaly, we will first consider the closely related question of the α–β transitions in tectosilicate minerals, which are accompanied by marked changes in macroscopic properties such as volume (Fig. 3). It is now agreed upon that these transitions represent the

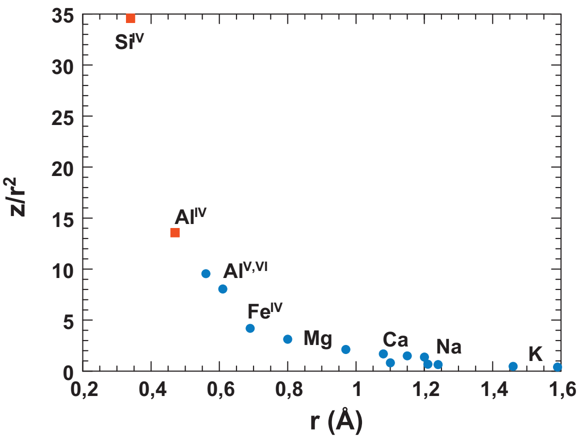

Fig. 2. (Color online.) Decrease with cation radius of the strength of bonds between cations and oxygen as given by variations of field strength, z/r^2. Radii for Si, Al and Fe in the IV- or VI-fold coordination indicated; for alkalis and alkaline earths in coordination states ranging from 6- to 8-fold (radii from Whittaker and Muntus, 1970).