

## The special situation of silicon

All beginning Earth-science students can tell you that silicon is important. After all, it's the most abundant cation-forming element in Earth's crust, and thus we have many silicate minerals that make up the bulk of the crust. However, such students may not realize that silicon, or more specifically the  $\text{Si}^{4+}$  cation that it almost inevitably forms, is also a bit peculiar. The peculiarities of  $\text{Si}^{4+}$  ultimately result from where it's situated in the periodic table.

Let's start by looking at the peculiarities. We're all taught that quartz ( $\text{SiO}_2$ ) is a very stable and insoluble mineral. After all, it's the mineral at the bottom of Goldich's Weathering Series, hanging around after other silicates have

weathered, and thereby becoming the dominant mineral of many sands. *However*,  $\text{Si}^{4+}$  is also the fifth most abundant dissolved constituent of river water and the tenth most abundant dissolved constituent in deep ocean water, suggesting that it's relatively soluble.

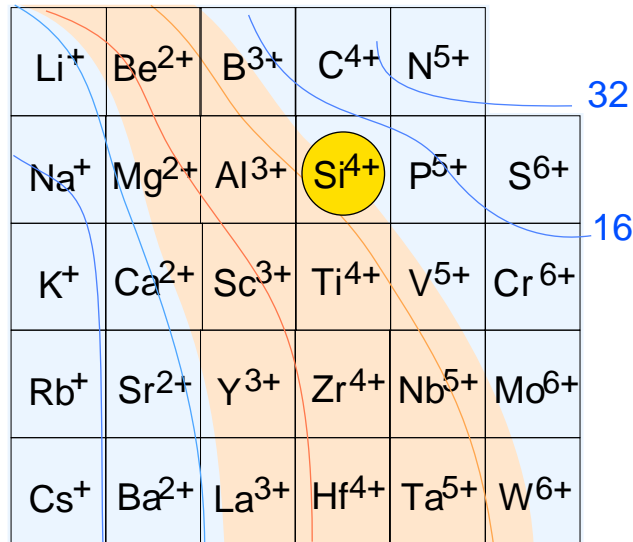
If that's the low temperature side of the story, consider the opposite extreme. In high-temperature Earth-science, we encounter  $\text{Si}^{4+}$  as the most abundant cation of almost all magmas. In fact,  $\text{SiO}_2$  is 30% to 80% by weight of most silicate magmas. *However*, minerals rich in  $\text{Si}^{4+}$ , and especially  $\text{SiO}_2$  minerals, are among the last to form in the crystallization of magmas. One is thus left with the paradox that silicon is a relatively incom-

patible element in the crystallization of silicate magmas. That happens, for the most part, because of repulsions between  $\text{Si}^{4+}$  cations (see this book's pages on Bowen's Reaction Series for more on that).

If that's a geological look at  $\text{Si}^{4+}$ , let's consider it biochemically. One characteristic of terrestrial nutrients like  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{K}^+$  is that they're sufficiently soluble to pass from soil waters into the roots of plants and then move in solution upward through those plants.  $\text{Si}^{4+}$  does that too. *However*, many plants then store  $\text{Si}^{4+}$  as phytoliths of opaline silica within their tissue. They thus convert dissolved  $\text{Si}^{4+}$  into a solid mineralized form, something they do with no other cation. Once again, we see the split personality of  $\text{Si}^{4+}$ , seemingly soluble and mobile in solution, and seemingly insoluble and stable as a solid.

So what do all these "peculiarities" have to do with where  $\text{Si}^{4+}$  is situated on the periodic table? The ionic potential of  $\text{Si}^{4+}$ , about 9.76, puts it at the threshold between insoluble cations like  $\text{Al}^{3+}$  and  $\text{Ti}^{4+}$  and soluble cations like  $\text{C}^{4+}$  and  $\text{P}^{5+}$ . In high-temperature terms, it's at the threshold between compatible or refractory cations like  $\text{Al}^{3+}$  and  $\text{Ti}^{4+}$  and incompatible or volatile cations like  $\text{C}^{4+}$  and  $\text{S}^{6+}$ . That position at the threshold means that  $\text{Si}^{4+}$  is not just exceptionally abundant: it's also distinctly ambivalent in its geochemical behavior.

### Contours of ionic potential:



$\frac{\text{charge}}{\text{radius}} = \text{ionic potential}$   
 e.g., for  $\text{Si}^{4+}$ ,  $r = 0.41 \text{ \AA}$ , so  $\text{i.p.} = \frac{4}{0.41} = 9.76$

### Conceptual model of the behavior of oxides of hard (and intermediate) cations

