Tilts without tears – Structure and elasticity of feldspars

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Framework structures such as feldspars and perovskites typically respond to changes in pressure, temperature and the extra-framework cations by the tilting of the strongly-bonded polyhedra, with little change in the geometry of the individual polyhedra. In the perovskites, the complex tilt patterns can be decomposed in to a combination of six fundamental tilts [1] that have been shown to act as the order parameters that relate the structural evolution of perovskites to their thermodynamic and elastic properties [2]. Tilts are therefore the appropriate fundamental description for the evolution of framework structures.

By contrast, structural variation in feldspars has only briefly been described in terms of tilts [3], and instead work for the last 3.5 decades has focussed on the variation of the T-O-T angles despite these showing very few or no systematic correlations with thermodynamic properties. The complexity and low-symmetry of the feldspar framework, which means that the tilts are not symmetry-breaking and are also difficult to model, is probably the reason for this neglect of tilting. In this contribution I will describe the decomposition of the variation of the feldspar structure in to the four fundamental tilts that were previously defined by Megaw [3], and the construction of an exact rigid-body model of the framework that can be used to show how the various tilts change the unit-cell parameters. This model explains the unit-cell parameter variations seen in real feldspars, and the extreme anisotropy of the response of the feldspar structure to changes in temperature, pressure and extra-framework cation. The success of this analysis offers the opportunity to develop a structure-based model for the thermodynamic and geochemical properties of feldspars in general.

[1] Glazer (1972) *Acta Cryst* **B28**, 3384-3392. [2] e.g. Carpenter *et al*. (2005) *Phys Rev B* **72**, 024118; Wang & Angel (2011) *Acta Cryst B,* in press. [3] Megaw (1974) in "The Feldspars", eds Mackenzie & Zussman.

Available-phosphate oxygen isotopes point to extracellular equilibration

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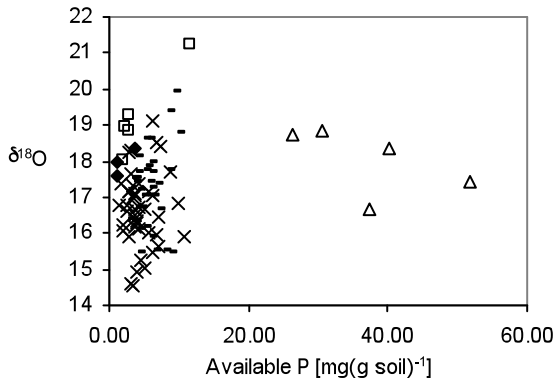
The oxygen stable isotopes in phosphate which is rapidly available for biological uptake can be used as a tracer for phosphorus cycling. Using this tracer in the ocean and in soils requires good understanding of the processes that control it. Here we present the first survey of available (resin-extractable) inorganic δ^{18}Op, based on a method we have recently developed [1]. This survey took place across natural and experimental rainfall gradients, and across soil formed on sedimentary and igneous rocks. In addition, we also analyzed the soil total (HCl-extractable) inorganic δ^{18}Op. The available-P values were in the range of 14.5-21.2‰ (Fig. 1).

Figure 1: Range of concentrations and $\delta^{18}O_p$ at five sites, with annual rain fall varying between 90-780mm/y. A site with igneous bedrock is marked by triangles.



The observed available-P δ^{18}Op values are considerably higher than the values we calculated (based on [2]) for extracellular mineralization of organic phosphate. However, these values are close to the value expected for enzymatic mediated phosphate equilibration with soil water. Evidence for equilibration was also reported in ocean studies, and was usually attributed to fast microbial recycling. However, we argue that microbial recycling can explain equilibration only if inorganic-phosphate excretion overwhelms other fluxes in the system. As a result, we conclude that the equilibration can be better explained by activity of extracellular pyrophosphatase.

[1] Weiner *et al*. (2011) *RCM* **25**, 624–628. [2] Liang & Blake (2009) *GCA* **70**, 3957-3969.