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Equilibrium and Kinetic Properties of Minerals

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How can the equilibrium and non-equilibrium thermodynamics of minerals be understood from their atomic-scale structural features? How can they be predicted, simply from models for the forces between atoms? Advances in analytical theory, statistical mechanics, experimental solid-state science, computational power, and the sophistication of a mineralogical approach that brings all of these together, means that these questions, once imponderable, are now realistically tractable. These questions have been exercising the minds of mineralogists over the last decade or so, and have motivated many developments in the science. Acting as way-markers along the path, there are a number of publications which have followed from meetings where these questions have been addressed. It is now twelve years since the publication of *Microscopic to Macroscopic*, an edition of *Reviews in Mineralogy* (Kieffer and Navrotsky, 1985) that sought to identify the fundamental controls on the bulk properties of minerals in terms of their atomic-scale characteristics. Since then there have been further rapid and significant advances in the field, which have been reflected in a number of additional meetings and subsequent volumes. One such was the NATO ASI meeting on *Physical Properties and Thermodynamic Behaviour of Minerals* (Salje, 1988). A more recent meeting, on what might be thought of as a related theme, was the Mineralogical Society Winter meeting on *Stability of Minerals*. Held at UCL in December 1989, this was published as one of the Mineralogical Society monographs (Price and Ross, 1992). The area of the surface science of minerals has entered the arena more recently still, represented in the same way by the volume by Vaughan and Pattrick (1995), also arising from a Winter Meeting. This issue of *Mineralogical Magazine* provides another marker of progress in the field.

The following eight papers give a small sample of the progress that has been made in the understanding of the equilibrium and non-equilibrium properties of minerals more recently. They represent a selection of the scientific discourse that arose under the umbrella heading of ‘Equilibrium and Kinetic Properties of Minerals’ during the meeting that was held in Cambridge in January 1997. This event saw the coming together of over two-hundred participants over three days, during which the links between the microscopic, the mesoscopic and the macroscopic features of minerals were addressed in the form of around sixty presentations. Abstracts of all the presentations have appeared in *Journal of Conference Abstracts*, volume 2 (1997). The papers published here give some flavour of the event, and are indicative of the areas in which progress has been made since the UCL and Manchester winter meetings. The scope of the papers reflects that of the meeting, tackling issue of mineral stability and instability in environments ranging from the mantle to the surface, probing the underlying driving forces for displacive transitions, order-disorder behaviour, reconstructive transitions, and chemical reactions within and between Earth materials.

The first of these papers, by **Warren** *et al.*, illustrates the increasing contribution to our understanding of the Earth that is provided by ab initio electronic structure calculation. The transition pathways between cubic, tetragonal, and orthorhombic silicate perovskite have been studied by first principles calculations, directly linking the structure to the energies of phases. Combining molecular dynamics simulations with the quantum mechanical results, the orthorhombic structure of $MgSiO_3$ is predicted to remain stable along the mantle geotherm. **Azough** *et al.* have adopted a simpler, empirical, model for the forces between atoms in silicates to investigate the mechanisms by which cations in pyroxenes exchange. They calculate energies for migration of Ca and Mg in diopside, which can be related to experimental measurements of bulk diffusion in single crystals. Thereby, they show how atomistic computer simulation can be employed to shed light on experimental results, aiding the interpretation of macroscopic measurements in terms of microscopic mechanisms.

The nature of cation exchange in mantle minerals is further explored in the study by **Redfern** *et al.* of Fe-Mn order/disorder over the M-sites of olivine. Here, neutron diffraction has been used to probe the structural states of olivine to high temperatures *in situ*. The kinetics of the exchange process are too fast for the high-temperature states to be retained during quench, and hence, in this case, the kinetics of the process have, until now, precluded the study of the thermodynamics of order-disorder in olivine. A mean-field Landau model for the order-disorder is applied successfully to describe the response of the structure to temperature. **Kerschhofer** *et al.* also adopt experimental mineralogical methods to study processes of change in olivine (α), but this time the reconstructive transitions to wadsleyite (β) and ringwoodite (γ) as a response to both temperature and pressure increase. The kinetics of the α-β-γ transformations are found to be strongly dependent on the microscopic mechanisms of nucleation of β and γ, in particular whether the nucleation of these phases within olivine is mediated by stacking faults within the olivine structure, as revealed by microstructural studies. The role of viscoelastic relaxation and elastic strain energy is found to be significant, given the large volume changes at each transformation in the system. The link between local defect structures, inhomogeneous fluctuations and strain relaxation is further explored in the case of alkali feldpsars by **Hayward** *et al.* By measuring diffuse X-ray scattering the strain field associated with ferroelastic twin walls has been determined quantitatively, for the first time. The length scale of the strain field is similar to that associated with a point defect on the M-cation site, and has been used to explain the nature of the high-temperature phase boundary between triclinic and monoclinic feldspars. Ginzburg-Landau theory has been exploited to explain the temperature-dependence of the domain wall thickness, as observed from scattering experiments.

The kinetics of high-temperature transformations in clays are also shown to be amenable to study by fast X-ray diffraction in the work of **Bray** *et al.*, who take advantage of the unique characteristics of synchrotron radiation to chart the dehydration of swelling clay at high - temperature over time scales of a few seconds. It is found that, when far from equilibrium, the rapid readjustment of the clay structure to a less hydrous state is accompanied by significant structural heterogeneity. The link between non-equilibrium behaviour and inhomogeneous transformation is once more made, demonstrating that the fundamental physics of the equilibrium and kinetic behaviour of minerals is applicable in environments ranging from the transition zone of the mantle to sedimentary basins. **Skipper** reviews the insights provided to complex clay mineral systems by computer simulations of clay-fluid interactions. Molecular modelling studies of smectite–water interactions at pressures corresponding to burial depths of up to 9 km provide predictions of the relative stabilities of fully and partially hydrated systems. Thus he is able to link the geological observation that illite forms at burial depths of 1.5 km or more to calculations of the density of clay structures provided from models for fundamental interatomic interactions. A final review of the insights provided by first-principles quantum techniques in the study of molecular processes at mineral surfaces by **Gillan** *et al.* brings us back full circle to our starting point. The growing importance of dynamical first-principles simulation to the study of surface chemical reactions on oxides is illustrated, using methods closely related to those employed by **Warren** *et al.* in their study of deep Earth phenomena. Thus we see the range and scope of the methods employed to elucidate the physics and chemistry of mineral stability, and the ways in which cross-fertilisation across the physical sciences is advancing and enlightening the mineral sciences.

Finally, it is interesting to note the contribution made by the growing availability of large computing resources. Of these papers, half are based on computational mineralogy, which continues to develop rapidly as increasingly complex problems become accessible using ever more sophisticated computational methods. The papers representing experimental mineralogy reflect the importance of national and international science facilities to mineralogy, including neutron and synchrotron radiation sources and international collaboration at laboratories such as the Bayerisches Geoinstitut. No increase in computing power, sparkling new analytical instrument or wonderful experimental facility can, of itself, generate significant advances in our understanding of the Earth, however. Such understanding relies upon the scientific wit and imagination of the protagonists, and evidence for the health of the body scientific in this area is clear, not least from the following contributions.

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