MODELLING IR ABSORPTION FOR Si–O STRETCHING VIBRATIONS OF 2:1 LAYER SILICATES BASED ON BOND VALENCE CALCULATIONS

VÁCZI, T., TÓTH, E. & WEISZBURG, T. G.
Department of Mineralogy, Eötvös Loránd University, Pázmány Péter sétány 1/C, H-1117 Budapest, Hungary
E-mail: thomas@ludens.elte.hu

A simple bond valence model was set up in order to aid the decomposition of Si–O vibrations in the infrared spectra of 2:1 layer silicates. Most of these infrared spectra do not show a single absorption band but rather show a more or less complex distribution of absorption wavelengths and intensities. The decomposition can be quite ambiguous as there can be a high number of different cation environments present. Our assumption in the model was that bulk chemical composition is a sum of different local compositions without any ordering constraints. This is of smaller importance for ordered structures (there are few different local arrangements) but a high degree of disorder means there is a distribution of many possible local arrangements, each contributing to the IR absorption spectrum. The present model tries to give a method for the decomposition of the tetrahedral Si–O stretching region at around 1000 cm^{-1} in the infrared spectrum.

In this model the Si–O bonds in one “central” SiO_4 tetrahedron of a *T* sheet is modelled. All possible first-cation environments, including interlayer (*IL*) and octahedral (*O*) ones, were taken into account and their contributions to the central Si–O bonds were calculated. One oxygen in each tetrahedron is bonded to the *O* sheet and is called apical, while the other three are shared with three neighbouring tetrahedra in the *T* sheet and are called basal oxygens. To cover all 2:1 layer silicates vacancies were allowed in *IL* and *O* positions. All cations were represented by their formal charge.

The bond valences for each silicon–basal oxygen bond were calculated using the first tetrahedral neighbour and two *IL* cations (the latter in 12-fold coordination). Tetrahedral neighbour cations included Si^{4+} and Al^{3+}, while only single charges (i.e., monovalent cations such as K^+, Na^+) were considered in *IL* positions. The cation environments in the modelled neighbourhood ranged from 3Si to 3Al and 0K to 3K, giving 32 possible configurations.

The bond valence for the apical oxygen was derived from all possible arrangements of divalent cations (M^{2+}), trivalent cations (M^{3+}) and vacancies for 3 octahedral positions, not excluding highly unlikely associations such as 3 trivalent cations or 3 vacancies as well. The orientation of the *O* arrangements relative to the tetrahedral sheet was ignored as only a single (apical) oxygen bridges the *O* sheet to the central tetrahedron. This setup gave 10 octahedral arrangements for each *T*–*IL* combination, thus a total of 320 neighbourhood configurations of a single SiO_4 tetrahedron are evaluated in the model.

Each Si–O bond valence is calculated independently from the other three using the relevant neighbouring cations’ contributions. The resulting four bond valence values (3 basal and 1 apical) are then scaled to give a sum of 4 to match the charge of the central Si.

To represent chemical composition, each of the 320 configurations was assigned a weight factor calculated from the relative occupancies of cations in each of the three types of cation positions (*IL*, *T*, *O*). Relative occupancy (RO) is the ratio of the number of the given cation p.f.u. and the number of hosting cation positions per 22 negative charges. The sum of the relative occupancies of all cations and vacancies in a given type of cation position is by definition always 1. The weight factors are then calculated by multiplying appropriate relative occupancies for any given configuration. This is done 320 times, giving a distribution of probabilities of occurrence for 320 sets of four bond valence values.

The four Si–O bonds in each of the 320 configurations give 216 unique bond valence values. The weight factors associated with each bond valence value are summed up and plotted as bond valence–probability diagrams. In this paper we present calculated plots for several ideal and realistic layer silicate compositions ranging from talc and pyrophyllite through smectites to dioctahedral and trioctahedral micas. The diagrams are qualitatively compared with experimental IR spectra of minerals of equivalent compositions, based on the assumption that bond valences are related to bond lengths and therefore to IR absorption bands. The model gives promising results for phases with low *IL* occupancy. For high *IL* occupancies some further refinement is needed.