A4-6: Data Bank for Pressure Computations of Amphiboles from Their Al$_t$

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In this study, crystal structures of amphiboles from various places in the world are used. In these calculations, it is assumed that the tetrahedral sitesnot filled by Si are occupied by Al, and the remaining Al atoms are in octahedral co-ordination. However, for pressure calculations Al$_t$ is used.

We computed pressures (kbar) from Al$_t$ using the following equations:

$P_{HZ} = -3.92 + 5.03$ Al$_t$,

$P_H = -4.76 + 5.64$ Al$_t$, and

$P_{JR} = -3.46 + 4.23$ Al$_t$.

In our data bank we have over 500 amphiboles and all three equations have been applied to each amphibole mineral. Where the quantity of Al$_t$ is insufficient, the pressure equation showed a negative value. The pressure data of the amphiboles evaluated statistically are help to classify them as very low pressure, low pressure, medium pressure and high pressure amphiboles.

We hope that this data bank will help volcanic petrologists to make predictive models.

A4-7: Neutron Diffraction and Li MAS-NMR Study of the Amblygonite (LiAlPO$_4$F)-Montebrasite (LiAlPO$_4$OH) Solid Solution

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The amblygonite-montebrasite minerals show complete solid solution with ideal composition LiAlPO$_4$(F,OH). We used neutron powder and single-crystal diffraction and Li MAS NMR to study the effect of F>OH substitution on the series. Lattice parameters for single crystals show increasing b and decreasing a, c, and V with increasing F/(F + OH). The volume is highest for the OH end-member because of the Al atom. The a and c parameters decrease with increasing F/(F + OH) because the O-H vector is close to the a-c plane and the Al-OH/F vectors are approximately parallel to it. Lattice parameters refined from neutron powder diffraction patterns collected at lower T show that thermal contraction increases with F/(F + OH), presumably because the F anion takes up less space than the OH molecule.

As shown in previous studies, the Li displacement ellipsoid becomes extremely large and anisotropic with increasing F fraction. U$_{eq}$ values corresponding to the Li atom increase show a greater reduction with decreasing temperature than the other atoms. The temperature dependence of Li is the same regardless of F content. The large intercepts at zero temperature for the Li atomic displacement parameter imply a large static disorder. The disorder in the Li site is obviously caused by the substitution of F for OH. The driving force is the loss of the hydrogen bond to O4, which causes the Li-O4 bond to strengthen and improves the bond valence to O4. The results show that the H atom position is imbedded within the distorted octahedral oxygen co-ordination of the Li atom. When a split Li site is used to better model the disorder, the results show that Li1 occupancy decreases and the Li2 occupancy increases with increasing F content, and the Li1-Li2 distance is longer for intermediate compositions than for the end-members.

Li MAS NMR spectra of samples with F/(F + OH) values >0.08 clearly showed two signals. The relative intensities of the two peaks corresponds to the occupancy of Li1 and Li2 positions. Spectra collected at temperatures up to 403 K show little change, indicating that there is no exchange of the Li ions between the two sites over

this temperature range. This shows that at a given site there is a specific location for the Li ion, determined by F or OH occupancy at the OH/F site. The disorder observed is the summation of these two locations over the crystal.

A4-8: The stability of alluaudite in granitic pegmatites: a study of the Na$_2$(Mn$_{1-x}$Fe$^{2+}_x$)$_2$Fe^{3+}(PO$_4$)$_3$ solid solution

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Alluaudite, a Na-Mn-Fe-bearing phosphate mineral, is known to occur in Li-rich granitic pegmatites. During the past decade, several compounds with the alluaudite structure were synthesized, but their stability was scarcelyconsidered. Because alluaudite can occur as a primary phosphate in granitic pegmatites, we decided to investigate the stability of the Na$_2$(Mn$_{1-x}$Fe$^{2+}_x$)$_2$Fe^{3+}(PO$_4$)$_3$ solid solution, with chemical compositions corresponding to that of unoxidized alluaudites.

The hydrothermal syntheses were carried out between 400 and 800°C at 0.1 GPa, using horizontally arranged Tuttle-type cold-seal bombs. The oxygen fugacity was controlled by the Ni-NiO buffer. Pure alluaudite is obtained at 400 and 500°C, whereas the association alluaudite + maricite appears between 500 and 700°C. The upper stability limit of alluaudite is defined by the crystallization of maricite, because this mineral has never been observed in granitic pegmatites. This limit corresponds to 550-600°C for Na$_2$Fe$^{2+}_2$Fe^{3+}(PO$_4$)$_3$, and to 450-500°C for Na$_2$MnFe^{2+}Fe^{3+}(PO$_4$)$_3$.

At 800°C, alluaudite and maricite are associated with an undetermined phase, whereas fillowite crystallizes above 600°C, in the Mn-rich part of the diagram.

Electron microprobe analyses of the synthesized phosphates were also performed, in order to establish phase relations in the central part of the Na-Mn-Fe (+PO$_4$) ternary diagram. When the temperature increases from 400 to 800°C, the composition of alluaudite shifts towards the Na-poor part of the diagram. This behaviour is related to the crystallization of maricite, a phase richer in Na than alluaudite.

Finally, experiments were carried out using the Fe$_3$O$_4$-Fe$_2$O$_3$ and Cu$_2$O-CuO oxygen fugacity buffers. Whereas the association alluaudite + maricite is observed with the Ni-NiO buffer, the Fe$_3$O$_4$-Fe$_2$O$_3$ buffer produces the crystallization of pure alluaudite. Under the high oxygen fugacity fixed by the Cu$_2$O-CuO buffer appears the association alluaudite + hematite, which indicates a complete oxydation of iron.

A4-9: A Temperature-Resolved Synchrotron X-ray Diffraction Study of Thermal Decomposition in End-member and Cation-Exchanged Hydrotalcite

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In the family of hydrotalcite minerals, trivalent cations within brucite-like octahedral sheets generate a net positive charge that is electrostatically balanced by anionic groups in the interlayer. It has long been known that these so-called anionic clays will readily exchange their interlayer species, but recently Komarneni et al. (1998) made the surprising observation that these clays also can remove significant quantities of dissolved transition metal cations in solution, such as Co^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+}, at room temperature. Based on their measurements of changes in fluid chemistry, these authors argued for a direct exchange between the transition metals in solution and the structural Mg cations that compose the octahedral sheets.

Our Rietveld analyses of metal-exchanged hydrotalcite using synchrotron X-ray powder diffraction support the proposed exchange model.