Tandem LA –LIBS Analysis for Determination of P, F, Ca, Na, Cl and Trace-level REE in Apatite.

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Phosphorus is the main element in fertilizers for food production as well as an important ingredient for water and metals treatment, in detergent and toothpaste production, and in the battery and lamp manufacturing. It is obtained from mining of phosphate rocks, mostly of minerals belonging to the apatite group (Pufahl and Groat, 2017). Although the most import minerals in the apatite group are calcium phosphates with the simplified formula $(PO_4)_3X$, where X=F, Cl, OH, there is a very large range of substitutions for Ca (Ca^{2+}, Pb^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}, Na^{+}, REE^{3+}, Bi^{3+}) and P (CO_3^{2-}, SiO_4^{4-}, $S0_4^{4-}$, VO^{-}, AsO^{-}), derived from charge compensation of the different atoms (Pasero et al., 2010). There is no consensus for the location of the CO_3^{2-} and OH^{-} groups in the apatite structural formula, as the direct analysis of such anionic groups is difficult. CO_3^{2-} is usually admitted, substituting for the phosphate anion (called type B substitution), but it has also been detected in the X position, called type A apatite (Comodi and Liu, 2000). Apatite composition and the complex substitutional scheme affect the mineral’s properties much more than the obvious phosphate grade attainable in a concentrate: its solubility, reactivity and its effect on apatite geochronology (Hughes and Rakovan, 2015), its surface chemistry (Chairat et al., 2007) and therefore floatability (Barros et al., 2008) (Horta et al., 2016).

While LA-ICP-MS has been used to detect and measure trace level REE’s and transition metals in apatite minerals, the precise determination of phosphorus and halogen elements in apatite and other minerals has proven difficult by traditional methods of scanning electron microscopy (SEM-EDS) and laser ablation ICP-MS (LA-ICP-MS). In this study, we present Tandem LA –LIBS analysis that combines both Laser Induced Breakdown Spectroscopy (LIBS) and LA-ICP-MS for detection and measurement of P, F, Ca, Na, Cl in apatite minerals as well as REE’s and transition metals. The Tandem LA –LIBS technique is an emerging in-situ analytical technique in geoscience to fully characterize the chemistry of halogen and hydrous minerals.

References

Barros, L.A.F., Ferreira, E.E., and Peres, A.E.C. (2008) Floatability of apatites and gangue minerals of an igneous phosphate ore. Minerals Engineering, 21(12-14), 994-999.

Chairat, C., Oelkers, E.H., Schott, J., and Lartigue, J.-E. (2007) Fluorapatite surface composition in aqueous solution deduced from potentiometric, electrokinetic, and solubility measurements, and spectroscopic observations. Geochimica et Cosmochimica Acta, 71(24), 5888-5900.

Comodi, P., and Liu, Y. (2000) CO3 substitution in apatite: further insight from new crystal-chemical data of Kasekere (Uganda) apatite. European Journal of Mineralogy, 12(5), 965-974.

Horta, D., Monte, M.B.d.M., and Leal Filho, L.d.S. (2016) The effect of dissolution kinetics on flotation

response of apatite with sodium oleate. International Journal of Mineral Processing, 146, 97-104.

Hughes, J.M., and Rakovan, J.F. (2015) Structurally Robust, Chemically Diverse: Apatite and Apatite Supergroup Minerals. ELEMENTS, 11(3), 165-170.

Pasero, M., Kampf, A.R., Ferraris, C., Pekov, I.V., Rakovan, J., and White, T.J. (2010) Nomenclature of the apatite supergroup minerals. Eur J Mineral, 22(2), 163-179.

Pufahl, P.K., and Groat, L.A. (2017) Sedimentary and Igneous Phosphate Deposits: Formation and Exploration: An Invited Paper. Economic Geology, 112(3), 483-516.

Vignoles, M., Bonel, G., and Bacquet, G. (1982) Physicochemical study on phosphocalcium carbonated apatites similar to francolite. Bulletin de Minéralogie, 105, 307-301.

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