Sample preparation and multi-element analysis of geological materials by HR-ICP-MS: an application to the building stones of the Roman Theatre in Catania (Italy)

PUNTURO R., CENSI P., LO GIUDICE A., PEZZINO A.

Dipartimento di Scienze Geologiche, Università degli Studi di Catania, Italy, (punturo@mbox.unict.it)

The knowledge of the compositional characteristics of stones used for the historical buildings is a key tool for a successful restoration. Nevertheless, the difficulty to recovery quantity of rocks suitable for laboratory investigation is one of the most severe limits for the studies inherent the grade of weathering and/or the provenance. For this reason, we tried to perform a fast, reliable and accurate method for the chemical characterisation of geological materials by using small amount of sample. The method deals with rocks of interest in the field of Cultural Heritage and in Earth Sciences. It involves sample dissolution and trace elements determination in various rock matrices. In order to validate the method, we studied a number of international geo-standards: andesite (AGV-1), basalts (BHVO-1 and BCR-1), marine mud (MAG-1) and diorite gneiss (SY-4). The preparation procedure involved acid decomposition at controlled Pressure (Pmax=400psi) and Temperature (Tmax=230°C) in a microwave apparatus (MARS5, CEM Technologies). Elements occurring in trace levels such as Y and REE, 3-D transition elements and some HFSE (e.g. Zr, Nb, Sr) were measured at ng g^{-1} levels with a magnetic sector HR-ICP-MS (Element2, ThermoFinniganMAT, Germany). After accurately optimised the instrument parameters, the procedure involved the separation of the interfering peaks from the analytes of interest by choosing the optimum resolution for each element with regards to its abundance in the rocks. Further in the work, the interest was focused on the suppression of matrix effects. Each standard was digested at least three times and more measurements were carried out on each solution obtained. A set of digestions and measurements on sample SY-4 showed that the time of acid attack as well as acid proportions must be different for this rock matrix, since refractory minerals occur. Laboratory data showed good agreement with data from literature. The method proposed for routine measurements was applied to the geochemical characterisation of granitoid rocks from the Roman Theatre in Catania (Italy).

Isotope evidences of PGE redistribution in the mantle

YU.D.PUSHKAREV[1], A.I.KOSTOYANOV[2] AND M.P.ORLOVA[2]

[1]IPGG, emb. Makarova, 2, St-Petersburg, 199034, Russia (Pushkar@YP3452.spb.edu)

[2]VSEGEI, Sredny prospect. 74, St-Petersburg, 199034, Russia (vsegei@email.wplus.net)

Isotope study of mafic-ultramafic rocks and associated with them platinum-group minerals (PGM) were carried out to estimate if there are any processes which are able to redistribute PGE in the mantle like some possible precondition before ore formation.

Rb-Sr and Sm-Nd isochron ages (122.6±1.5 Ma and 93±

47 Ma, respectively) as well as $(^{87}Sr/^{86}Sr)_0$=0.70393±5 and ε_{Nd}=+5.6 were determined for pyroxenite and gabbro-pegmatite from the Konder platinum bearing mafic-ultramafic massif. K-Ar ages of biotite (132±8 and 115±6 Ma) from ultramafic rocks and gabbro are in accordance with the above values. Sm-Nd results from ultramafic rocks are in disagreement with the isochron model and suggest the heterogeneous initial isotope composition of Nd. At the same time, a model initial isotope composition of Sr for dunite and olivine clynopyroxenite is identical to that for gabbro-pegmatite, pyroxenite and alkaline pegmatite. It shows common mantle source of all these rocks and confirms the same age of their origin. Lead isotopic composition in mafic (pyroxenite) and ultramafic (dunite, olivine clynopyroxenite) whole rock samples corresponds to that in young MORB and additionally supports their comagmatic origin. Os isotope composition was determined directly in platinum minerals enriched in Os. Compositions obtained turned out to be the same in five different samples having ($^{187}Os/^{188}Os$)=0.1251± 0.0003. If we suppose, that the age of platinum minerals is identical to that of mafic-ultramafic rock this value suggests an unusual source for the ore-bearing melt; which could be different from the mantle reservoir (identical to CHUR) by significantly lower Re/Os ratio. This might be explained by migration of Os and other PGE into the mantle substrate long before melting.

Various samples of PGM in ophiolites from Kamchatka-Karyakia region show distinctly heterogeneous Os isotope composition. There are discrete repeating values of $^{187}Os/^{188}Os$, which correspond to various discrete Re-Os model ages in the same rock. It seems that these ages demonstrate periodically repeating formation of PGM due to metasomatic redistribution of PGE in the mantle.

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