Silicon in sapphires – Its role and detectability by LA-ICP-QMS

A.H. SHEN

Gemological Institute of America, Laboratory, Carlsbad, CA 92008, USA (andy.shen@gia.edu)

Silicon is not known to create color centers in sapphire. In a blue sapphire, the coloring mechanism is well known to be the charge transfer between Fe^{2+} - Ti^{4+} pairs on neighboring sites in the lattice [1]. However, beryllium diffusion treatment in sapphire has forced us to examine the role of unusual non-coloring trace elements such as silicon. Emmett *et al.* [2] proposed that the difference between $[Mg^{2+} + Be^{2+}]$ and $[Ti^{4+} + Si^{4+}]$ concentrations directly affects the resulting color in a beryllium-diffused sapphire. LA-ICP-QMS (Laser ablation – inductively couple plasma – quadrupole mass spectrometry) has gained popularity among the gemological laboratories; therefore, the detectability of these non-coloring trace elements is an important issue. Among the elements in Emmett's model, silicon is the most challenging to analyze by ICPMS due to its omnipresence in the environment and isobaric interference. A series of experiments using single crystal synthetic and natural sapphires were performed to establish the detection limits and isobaric interferences of silicon isotopes while using LA-ICP-QMS. Three multiply-recrystallized synthetic sapphire crystals were used as 'true blanks' in these experiments and additional matrix related interferences were observed in ^{28}Si and ^{29}Si signals. Preliminary results indicated that, under ideal situation, a detection limit in the order of 100 ppmw is achievable. However, extreme caution is called due to lack of reference standards. The most commonly used NIST SRM glasses contains 32 – 33 wt % of silicon – well into analog mode operation of the multiplier - and interpolating such calibration to less than 100 ppm range can introduce dramatic errors. This is still a on-going project and the most up-to-date results will be discussed.

[1] Burns (1993) *Mineralogical Application of Crystal Field Theory*, 2nd Ed. Cambridge University Press, Cambridge, UK. [2] Emmett *et al.* (2003) *Gems & Gemology* **39**, 84–135.

Germanium/silicon ratios of diagenetic chert nodules in the Ediacaran Doushantuo Formation, South China

BING SHEN[1], CIN-TY LEE[1] AND SHUHAI XIAO[2]

[1]Dept. Earth Science, Rice University, Houston, 77005
[2]Dept. Geosciences, Virginia Tech, Blacksburg, 24061

Germanium/silicon (Ge/Si) ratios of dolostone-hosted chert nodules from the Ediacaran Doushantuo Formation (635~551 Ma) in the Yangtze Gorges area, South China are reported here. These chert nodules are precipitates formed by early diagenetic replacement of the host carbonate and are classified into two types based on their mineralogy and geochemistry. Type-1 cherts are pyrite-free, have low Al, and show a steep positive correlation between Al and Ge/Si with a zero-intercept. Type-2 cherts contain abundant pyrite, but show only slight positive correlation (with non-zero intercept) between Ge/Si and Al.

The Ge/Si-Al systematics are the result of mixing between pure chert (characterized by low Ge/Si) and an Al-rich endmember (characterized by high Ge/Si), the latter controlled by a clay component. However, Ge contents inferred for the Al-rich (clay) endmember are much higher than that expected for clay minerals alone, requiring another component that not only associates with clay but is also enriched in Ge. We speculate that such component may be represented by organic matter: organic matters can be strongly adsorbed by clays and certain organic molecules are known to have high affinity for Ge due to their strong metal ion-chelating properties. This interpretation is consistent with the geochemical differences between Type-1 and Type-2 cherts and the presence of pyrite in Type-2 cherts, which is indicative of bacterial sulfate reduction and anaerobic oxidation of organic carbon.

The steep positive correlations between Al and Ge/Si with zero intercepts of Type-1 cherts suggest that Ge in porewaters from which these cherts precipitated may have been dominated by Ge-organic complexes. The low Ge/Si inferred for the Al-rich endmember in Type-2 cherts are therefore taken to indicate lower concentrations of organic-bound Ge, perhaps due to anaerobic degradation of organic matter (accompanied by formation of pyrite) and redistribution of Ge between clay-organic endmembers and pure chert. These observations suggest that the aqueous depositional environment of the Doushantuo Formation may have been characterized by high DOC (dissolved organic carbon) content.