Insights into zircon U-Pb systematics from intercalibration with astronomical time

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High-precision U-Pb geochronology of accessory minerals is an integral part of various Earth Science disciplines. Recent advances in U-Pb geochronology by isotope dilution – thermal ionization mass spectrometry (ID-TIMS) allow dating of high uranium accessory minerals (most commonly zircon) at permil precision and external reproducibility. Such high temporal resolution may result in complex zircon age populations, reflecting prolonged growth, magma residence and/or zircon recycling, previously only resolvable by in-situ U-Th dating in Pleistocene magmatic systems. This allows to track the evolution of Cenozoic magmatic systems at unprecedented resolution and to add absolute time constraints to thermal and petrogenetic models. However, these complexities have also been considered to systematically bias zircon U-Pb derived eruption ages, to compromise chronostratigraphic applications of high-precision zircon U-Pb geochronology and to contribute to systematic offsets between the K-Ar and U-Pb systems [1,2].

Orbitally tuned Miocene sedimentary sequences around the Mediterranean contain abundant intercalated zircon-bearing ash beds. These sequences provide the rare opportunity to compare ash-bed zircon U-Pb dates with independent and accurate deposition ages derived from orbital tuning. This allows us to evaluate effects of prolonged crystallization and zircon recycling on zircon U-Pb derived ash bed deposition ages. We present a large data set (*N=18, n>200*) of high precision zircon U-Pb dates for ash beds from an almost continuous Messinian to Langhian (6.2-15.4 Ma) sedimentary sequence near Ancona, Italy [3, 4]. The majority of ash beds contain abundant zircons that predate eruption by several 10s to 100s of ka. However, considering only the youngest single zircon dates to interpret ash bed deposition, results in stratigraphycally consistent deposition ages that, for most of the section, agree with the astrochronologic age model. In the upper part of the section, we find an increasing offset between zircon U-Pb dates and astrochronologic age model within an ~8 m thick ash-rich interval. This may suggest that prolonged zircon growth and zircon recycling is more likely to bias U-Pb dates over short, ash-rich intervals where ash beds are likely derived from a repeatedly tapped, common magmatic source.

[1] Simon et al. (2008) *EPSL* **266**, 182-194. [2] Renne et al. (2010) *GCA* **74**, 5349-5367. [3] Hüsing et al. (2009) EPSL **282**, 140-157. [4] Hüsing et al. (2010) *EPSL* **290**, 254-269.

Temperature dependent structural changes in aluminoborosilicate melts with different modifier cations (Na, Ba, Ca)

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Introduction

Borosilicate glasses and melts are critical in technology. Because of the ease of transition among three- and four-coordinated boron with composition, temperature and pressure, they may also serve as analog system for silicates at high pressure. The effect of temperature on the structure of aluminoborosilicate liquids has been studied by ^{11}B, ^{17}O and ^{27}Al MAS NMR spectroscopy using glass samples prepared with different cooling rates and thus different fictive temperatures (T_f). The abundances of BO_3 groups and of non-bridging oxygens (NBO) increase with increasing T_f, indicating that the reaction $BO_4 \leftrightarrow BO_3 + NBO$ shifts to the right at a higher T. The modifier cation with higher cation field strength (Valence/square of ionic radius) promotes formation of BO_3 and NBO.
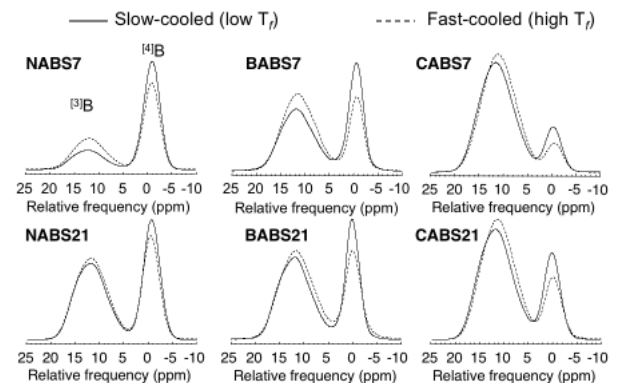
Figure 1: ^{11}B MAS NMR spectra at 14.1 Tesla. Dashed lines are samples with higher cooling rates. Solid lines are samples with low cooling rate. The peak centred around 12ppm is 3-coordinated boron, and the one centred around 0 ppm is 4-coordinated boron. The peak heights are normalized to constant total peak areas. The peak intensities are obtained by peak area integration. All the samples have 20 mol% of modifier cations (N for Na_2O, B for BaO, C for CaO), 8 mol% of Al_2O_3. The samples in first row have 7 mol% of B_2O_3, and 65 mol% of SiO_2; in the second row have 21 mol% of B_2O_3, and 51 mol% of SiO_2.

Conclusion

The observed *T* dependence of BO_4 species abundance allows us to estimate the enthalpy (ΔH) of the reaction $BO_4 \leftrightarrow BO_3 + NBO$ to be 20 to 50 kJ/mol in different glass compositions and closely related with the amount of NBOs in the glass. The ΔH is lower for the higher field strength network modifier cations ($Ca^{2+} > Ba^{2+} > Na^+$). This observation suggests that the divalent cations promote the formation of NBO much more effectively (lowers their enthalpy and thus free energy), which in turn helps to stabilize the modifier cation in the melt networks.