Color, stability, chemical durability and the environment of transition elements in oxide glasses

L. GALOISY[1*] AND G. CALAS[1]

[1]Sorbonne University, MNHN, UMR CNRS 7590, IRD, IMPMC, 75005 Paris, France (*correspondence : laurence.galoisy@upmc.fr)

Oxide glasses exhibit a complex structure. The diversity of the local structures around transition elements illustrates their original spectroscopic properties in these glasses [1]. By contrast to polyanions, in which the local geometry is generally well defined, cations may occur in a large diversity of local surroundings, which may give rise to radical modifications of their influence on the glass/melt properties (e.g. coloration processes, crystal/liquid element partitioning, nucleating behavior). The coordination numbers of transition elements in glasses are often lower than those in crystalline compounds. The short-range order is characterized by unusual coordination numbers, such as five-coordinated sites or tetrahedral sites, with the relative proportion of these sites depending on glass composition. 4-fold sites in glasses correspond to a network-forming position e.g. $^{[4]}Zn^{2+}$ [2] or $^{[4]}Ni^{2+}$ (that also induces a purple color in oxide glasses). The charge compensation of the tetrahedral cations by alkalis and/or alkaline-earths is important for rationalizing glass stability [3]. Original $^{[5]}Ni^{2+}$ and $^{[6]}Ni^{2+}$ explain the origin of the peculiar brown coloration of most Ni-bearing oxide glasses and the presence of Ni-ordered domains in low alkali borate and borosilicate glasses, respectively [4]. Regarding natural glasses, Fe-oxide nano-clusters are present in black natural glasses such as obsidians. These clusters show a specific local arrangement around Fe in these natural glasses, different from that encountered in industrial glasses [5] and related to the cooling history of the glass. Zr, is generally found in regular octahedra in oxide glasses, an unusual coordination seldom encountered in anhydrous minerals [6]. A molecular scale approach helps understand the origin of the peculiar physicochemical properties provided by the presence of Zr in glasses, e.g. the resistance to alteration [7].

[1] Calas *et al*. (2002) *C. R. Chimie* **5,** 831–843. [2] Le Grand *et al*. (2000) *J. Mater. Res*. **15-9,** 2015-2019. [3] Galoisy *et al*. (2005) *Phys. Chem. Glasses*, **46-4**, 394-399. [4] Galoisy (2006) *Elements* **2**-**5**, 293-297. [5] Vercamer *et al*. (2015) *JNCS* **428**, 138-145. [6] Jollivet *et al*. (2013) *JNCS* **381,** 40-47. [7] Jollivet *et al*. (2019) *JNCS* **503-504,** 268-278.