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The Crystal Chemistry of Complex Niobium and Tantalum Oxides: IV. The Metamict State: Reply

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In his discussion paper, Ewing has ably summarized the literature referring to radioactivity as a cause of metamict behavior. We are grateful to him for this emphasis, because it is clear from our paper that evidence for our "disproportionation" hypothesis is as yet rather sparse. However, our thinking was directed along these lines by a suite of twenty columbites and ixiolites from Western Australia which showed considerable variations in crystallinity in the absence of any observable radioactive elements.

Mineralogists have (with reason) grown up with the idea that isomorphous substitutions of almost unlimited extent are possible, and that isomorphous substitution in minerals is the rule rather than the exception (Bragg and Claringbull, 1965). On the other hand, solid state chemists and crystallographers have of recent years been elucidating various mechanisms for the accommodation of non-stoichiometry in oxides, most of which result in the formation of ordered stoichiometric phases, often closely related in structure so that the X-ray patterns simulate solid solutions (*e.g.*, Hyde *et al*, 1974). In mineral systems, among the most copiously documented is the unmixing of amphiboles and pyroxenes (Champness and Lorimer, 1973; Iijima and Buseck, 1974), but precipitation on a microscopic and submicroscopic scale is probably more common than has been supposed (Bennett *et al*, 1972; Nakazawa *et al*, 1974, Willaime, 1974; Graham, 1975).

Our proposal is that when submicroscopic precipitation is coherent, X-ray diffraction shows a crystalline material; when it is incoherent, the material may show a more or less amorphous X-ray diffraction pattern depending on the particle size and distribution of the phases.

It seems to us that Ewing's model of glass formation may be equivalent to ours at the limit of smallest particle size; the Russian literature has long emphasized that glasses are at least partly crystalline on the smallest scale and conditions for crystallization to form glass-ceramics are now well known. Both the glass structure and the microcrystalline structure are due to the supercooled state of the material. Some kind of differentiation could be attempted using electron diffraction, and in a preliminary study of a "disordered" ixiolite we have been unable to find any material which does not show a well ordered superlattice by this technique. The next step would be an investigation of fully metamict material.

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