

## An Oxygen Fugacity Grid For Nebular And Planetary Geochemistry.

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The quantitative characterization of the oxidation states for a broad range of multivalent elements in micrometer scale volumes is now possible using x-ray absorption near-edge spectroscopy (XANES). Such measurements can be used to determine, directly and precisely, the oxygen fugacity at which many geo/cosmochemically relevant reactions occur. With data available for a comprehensive suite of reactions, a grid of oxygen fugacity sensitive reactions boundaries can be assembled that provide fundamental constraints on nebular and planetary processes. The ability to constrain reactions directly in oxygen fugacity space removes a major limitation from thermochemical modelling of P-T-X relations as the need to make assumptions about the oxygen fugacity will be removed.

**INTRODUCTION:** The early nebula has provided samples that were produced under an enormous range of physical conditions. Among the most critical parameters that must be determined for many nebular and planetary assemblages is the oxygen fugacity (or the equivalent fugacity for the relevant buffer species) under which reaction occurred. Generally, oxygen fugacity is inferred indirectly, as techniques for directly measuring its effect were unavailable. However, the application of a new microanalytical technique (x-ray absorption near edge spectroscopy, or XANES) makes measuring the oxidation state of multivalent elements possible (1,2,3). The application of this technique to the estimation of oxygen fugacity (as well as the fugacity of other gaseous species) in terrestrial and extraterrestrial materials becomes an important constraint on models of nebular processes. Because quantitative measurements of oxidation state will permit detailed calculation of oxygen fugacity in a great variety of nebular and planetary reactions, it will be possible to erect a systematic grid of fugacity sensitive reactions, that bracket and constrain assemblages observed in chondrites and achondrites.

**Overview Of The Oxygen Fugacity Grid Approach:** Reactions involving change of valence in multivalent elements such as Fe (as well as Cr, Ti, Nb, V, Eu, Ce, U etc.) are controlled by the oxygen fugacity of the systems in which they occur. In some cases the fugacity is imposed by external gas reservoirs such as subsystems of H-C-O-S but in other cases the oxygen fugacity will be internally buffered by the solid-solid or solid-liquid reactions occurring (4). In both cases, however, the abundance ratios of different oxidation states for multivalent elements will be controlled in whole or in part by the oxygen fugacity and measurement of these abundance ratios directly constrains the ambient  $fO_2$ .

Because reactions involving these multivalent species occur throughout the range of probable nebular conditions, a grid of fugacity controlled reactions can, in principle, be created. A familiar subgrid of this oxygen fugacity grid is the  $fO_2$  vs temperature plot for the "classic" Fe-buffer curves: iron-wüstite; quartz-magnetite-fayalite; magnetite-hematite. Buffer reactions involving other elements and other phases also contribute to the complete grid. Reactions controlling the  $Fe^{3+}$ ,  $Fe^{2+}$  and  $Fe^0$  contents of coexisting phases will be among the most important and informative in both terrestrial and extraterrestrial systems as iron is generally high abundant and often ubiquitous in most systems. Reactions involving oxidation state changes for minor and trace elements are unlikely to influence the ambient oxygen fugacity of a system but will reflect that fugacity in their abundance ratios. Such reactions act as tests of inferred fugacity based on major elements and/or dominant gas species.

Temperature estimates can generally be made based on thermochemical data for a broad array of element partitioning reactions as reliable compositional data are available for many samples. Pressure estimates are more difficult especially for systems involving gases where the gas phase is lost. The pressures for nebular processes were generally low and the most sensitive indicator for these low pressure reactions, the gas/vapor phase is never preserved. An aspect of the pressure regime, the fugacity of the reacting gases may be accessible in some cases as the gas fugacity of the system controls the relative abundances of different oxidation states of some multivalent elements.

**Analytical Considerations:** Commonly used analytical techniques provide abundance data for a wide range of elements and isotopes, but provide no data, about the oxidation state of the elements in any phase. A typical analysis of a bulk chondrite will present the abundance of iron in the sample but provides no information about the abundances of ferrous, ferric and native iron that are summed

**Oxygen Fugacity Grid : Delaney, Sutton and Bajt**

together in that analysis. A few techniques are capable of measuring the ratios of the different valence states of elements. Mössbauer spectroscopy is the most widely used of these techniques but it is limited to relatively large samples and to elements for which appropriate isotopes are available. Techniques capable of measuring valence states of atoms in micro-scale volumes comparable with those of the standard microanalytical techniques have been unavailable. In addition, the previously available techniques can only be applied to a limited range of multivalent elements. An ideal technique would allow non-destructive measurement of the valence state of any element in a volume comparable with that analyzed by geochemical microprobes ( $\mu\text{m}^3$ ) so that both the variations within a single mineral grain and the partitioning of multivalent elements between coexisting phases can be measured. A technique for making these measurements is X-Ray Absorption Near Edge Spectroscopy (XANES) Applied With The Synchrotron X-Ray Microprobe (1). Although measurements carried out so far (1,2,3) have focussed on the elements Cr and Fe, this technique is applicable (in principle) to any element that occurs in multiple valence states. Oxidation state determinations using the microXANES technique is presently in its infancy but the potential exists for the development of a universally applicable method. The sensitivity of the technique is defined by the elemental concentrations and the brightness of available synchrotron x-ray sources. The accuracy is defined by the accuracy of interpretive methods for the XANES spectra and the availability of appropriate standards produced in experiments under controlled oxygen fugacity.

**Applications:** Elements whose variable oxidation states may be exploited as useful fugacity indicators include: Ti, V, Cr, Fe, Cu, Nb, Mo, W, (Ce,) Eu, U. Although the volatilities of most REE are sensitive to oxygen fugacity, the stabilization of multiple valence states in the solid phase (except Eu) may not be detectable. Terrestrial examples of the importance of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  measurements as part of the estimation of oxygen fugacity are well known (4,5). Extraterrestrial examples tend to be less obvious as systems involving ferric iron are less common. However, nebula conditions are so diverse that the existence of other elements in multiple oxidation states can be used to constrain oxygen fugacities in addition to Fe. Between the very reduced assemblages with  $\text{Si}^0$  stable in metallic phases to C-chondrite matrix with stable hematite and magnetite almost every multivalent element is likely to be present in different oxidation states. Some reactions with possible relevance to meteoritic assemblages include  $\text{Ti}^{3+}/\text{Ti}^{4+}$  in hibonite-fassaite assemblages and in various transition elements in refractory inclusions, rims, and feldspar;  $\text{Cr}^{3+}/\text{Cr}^{2+}$  exchanges in ol-pyx-spinel assemblages;  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in fine grained matrix material from C-chondrites, including alteration products in CI's, as well as partitioning between silicates and oxide minerals from chondrites and achondrites; and  $\text{Eu}^{2+}/\text{Eu}^{3+}$  exchanges in phosphate/feldspar/ pyroxene assemblages.

If several reactions involving oxidation state changes can be identified within a single assemblage, the intersection of reaction boundaries in temperature -  $f\text{O}_2$  space will define the P-T-X conditions under which reaction occurred. This approach cannot be yet be applied as there are insufficient data for oxidation state changes in natural materials. With the availability of synchrotron microXANES, the characterization of relevant reactions can be initiated. Systematic studies of the partitioning behavior of elements in multiple oxidation states must be carried out to identify the critical reactions in the oxygen fugacity grid so that it may be used in conjunction with existing petrogenetic, phase equilibrium and element partitioning results. For the classical Fe-buffers (Figure 1) most reaction boundaries have roughly parallel slopes. To maximize the sensitivity of the oxygen fugacity grid, it is essential that reaction boundaries intersect at high angles to these reactions be identified. Thus, buffering reactions that do not liberate  $\text{O}_2$  or other gases will be very important (i.e. reactions with very small volume changes.)

**References:** (1) Sutton et al.(1994) *this volume* ; (2) Sutton et al, (1993) *GCA* **57**,461; (3) Sutton et al. (1993) *LPSC XXIV*, 1385; (4) Carmichael & Ghiorso (1990) *Rev. Mineral.* **24**,191; (5)Ballhaus C.(1993) *Nature*, **366**, xxx : Acknowledgements: NAG9-304