

## Oxygen gas-phase formation in iron chemical gardens

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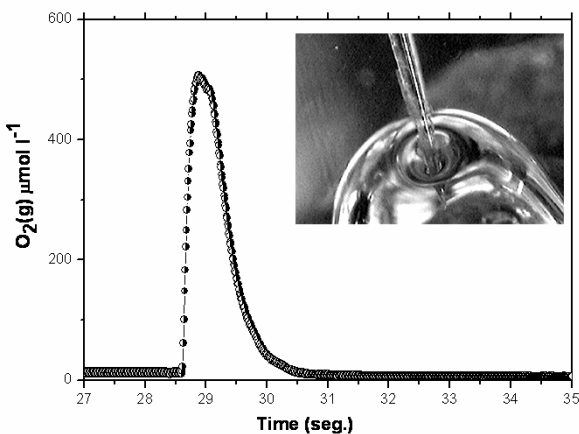
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In this work we have employed the chemical gardens reaction as a laboratory device for *in situ*, follow the mixing of aqueous solutions of iron salts with sodium silicate and to characterize the reaction products by SEM HREM, XRD and XPS.

Chemical gardens are well known tubular structures formed in reaction-precipitation systems given rise to the formation of colorful, plant-like aggregates. Moreover, recent investigations have contributed to a renewed scientific interest in these self-organised structures. Although the reaction in chemical gardens is largely driven by pH gradients between the dissolving iron salt and the Na-silicate, recent works suggest that a strong redox processes can also take place during the formation of iron-silicate membranes.

One intriguing aspect related with silica gardens formation is the presence of small bubbles that are, in some instances, attached to the surface of the silica membranes, thus acting as templates for the formation of hollow tubular structures.

The aim of this research was to experimentally verify the composition and mechanisms of bubbles formation on Fe-Silica garden. From experiments performed in strictly anoxic conditions we will show that O<sub>2</sub> gas bubbles are still formed inside the microtubular structures as result of redox surface reactions taking place during the formation of colloidal membranes. In situ determination of iron species by UV-VIS showed the presence of Iron(VI)-ferrate oxyanion. Thus, a model for O<sub>2</sub>-bubble formation in silica garden is proposed, based on the rapid reduction of Fe(VI) to Fe(III) species through the of the strong pH gradient taken place across the silica membrane. Implications of these results for the formation of Fe-silicate phases in anoxic sedimentary environments will also be discussed.



### Reference

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## The double-spike cookbook

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In recent years there has arisen considerable interest in exploring natural stable isotope fractionation of "non-traditional" elements. Here, the techniques of standard/sample bracketing or addition of a second element in the mass range (e.g. Cu with Zn) can be used on MC-ICP-MS instruments, but not TIMS. But the obvious method of choice in terms of accuracy – as well as simplicity in pre-separation chemistry – is to add a double spike (DS) of the same element to the sample. The DS "freezes in" the natural fractionation at the time of its addition, and is thereafter insensitive to any chemical or instrumental fractionation.

The natural fractionation is solved for via mass balance of 3 independent isotope ratios (effectively a 3D isotope space). The DS technique can thus be used for any element with four or more isotopes—or 33 elements in all. Nevertheless, it has been seriously underutilized, in part due to the unease of data reduction, but mostly from uncertainty in the choice of the double spike itself. The task is made all the more difficult from the sheer number of candidate double spikes and isotope spaces to consider. For example, for Fe there are only 4 such spaces, while for Sn, with its 10 isotopes, there are 840 possible isotope spaces. The rigorous "optimization" of any double spike problem, then, presents a formidable challenge.

What is presently hampering the widespread use of double spikes is a lack of a comprehensive solution to the problem. Here, I remedy the situation by tackling all 3868 isotope spaces of the 33 elements (201 isotopes) that can be double spiked. The approach yields (1) an estimate of the "best" mixture (M) to use within a given 3D isotope space (and its corresponding spike, S), along with (2) a "figure of merit" enabling comparison between different isotope spaces of each element. Together, these provide first-order answers to questions of what DS to use, what the optimal mixture is, and what isotope space yields the best error propagation? Exclusion of particular isotopes (e.g. isobaric interferences) becomes an easy task since all isotope spaces have been evaluated. The methodology contrasts with that of previous studies in two ways: first, the "optimal" mixture is explicitly solved for rather than the spike composition, and second, more rigorous criteria are used. Normal compositions (N) were taken from IUPAC. The "optimization" was performed by multi-dimensional numerical minimization using a penalty function approach. Four criteria are built into the function: (1) M should lie far from S and close to N, (2) the angle between the fractionation vector through N and the mixing line should be large, (3) the so-called "intersection angle" should be large, and (4) the absolute magnitudes of the 3 isotope ratios of M should lie close to unity. Once a promising DS has been identified, its performance as a function of spike-to-sample ratio can then be examined.

These calculations should remove a major obstacle to implementing the double-spike technique, and hopefully make its use more routine and *in vogue* in future stable isotope studies.