

## Reaction kinetics of aspartic acid solutions at elevated temperatures

J.S. COX AND T.M. SEWARD

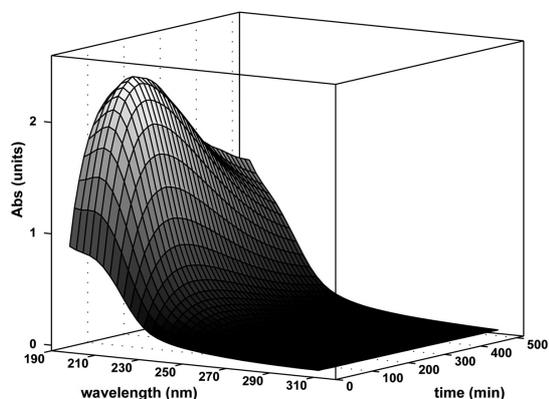
Institut für Mineralogie und Petrographie, ETH Zentrum, CH-8092 Zürich, Switzerland

The reaction kinetics of the breakdown of aqueous aspartic acid was first experimentally examined from a hydrothermal, non-enzymatic perspective by Vallentyne [1] and later in more detail by Bada and Miller [2-3]. Their studies have remained until now the most detailed experimental investigations of this system, with only a few broader qualitative studies having touched on aspartic acid in the interim.

We have been able to observe the reaction kinetics of aspartic acid *in situ* for the first time with a special spectrophotometric cell which is also itself the reaction vessel (Fig.1). The identities of the reaction products were further confirmed using ion chromatography (Dionex AminoPAC).

The pure aqueous aspartic acid system appears to be far more complex than previously understood. A postulated reaction scheme involving decarboxylation and deamination pathways will be presented and its dependence on temperature and other factors will be discussed. Rate constants for this scheme, derived mathematically from the experimental data using a factor analysis-based method, will be presented up to 200° C and 20 bar.

Figure 1: The decomposition of an aspartic acid solution at 176° C observed by UV spectroscopy.



### References

1. Vallentyne J.R. (1964) *Geochim. Cosmochim. Acta* **28**, 157-188.
2. Bada J. L. and Miller S. L. (1969) *J. Am. Chem. Soc.* **91**(14), 3946-8.
3. Bada J. L. and Miller S. L. (1970) *J. Am. Chem. Soc.* **92**(9), 2774-2782.

## Re-Os molybdenite analysis – Considerations for accurate and reproducible dates

ROBERT A. CREASER AND DAVID SELBY

Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta, Canada, T6G 2E3  
(dselby@ualberta.ca; rcreaser@ualberta.ca)

The  $^{187}\text{Re}$ - $^{187}\text{Os}$  geochronometer applied to dating molybdenite has been shown to yield accurate and precise dates, giving the timing of sulphide mineralization, information previously unattainable from other radio-isotope methods. Subsequently, the age data has aided in the improvement of the understanding of ore-systems. The establishment of Re-Os method for dating molybdenite requires a need to further understand the Re and Os isotope systematics in molybdenite.

Multiple Re-Os molybdenite analyses of identical polytype (2H), and of differing age, paragenesis and grain-size demonstrate Re and Os are inhomogeneous in molybdenite, and that  $^{187}\text{Re}$  and  $^{187}\text{Os}$  are physically 'decoupled'. This finding demonstrates that a homogeneous representation of all the Re and Os in the sample aliquot must be analysed to obtain an accurate Re-Os date and reproducible data. For example, molybdenite of ~5 mm grain-size was isolated to yield 7g of pulverized sample (44-210 $\mu\text{m}$ ). Analyses using 20-30mg gave a mean Re-Os date of  $370.9 \pm 0.7$  Ma (0.36% 2SD, n=5), in good agreement with  $^{40}\text{Ar}/^{39}\text{Ar}$  ages ( $368.6 \pm 6$ ,  $373.1 \pm 6$  Ma) of consanguineous muscovite. Analyses of the same sample using ~10mg returned dates outside analytical uncertainty, deviating by 3-4 Ma (~1%) from the mean Re-Os date. This effect of aliquot size on the obtained Re-Os date is also observed for Archaean molybdenite (Stein et al., 2001). For fine-grained (~1mm) Archaean molybdenite samples  $\geq 10\text{mg}$  is necessary to return accurate and reproducible ages, whereas coarse-grained (~1cm) Archaean samples require  $\geq 40\text{mg}$ . These data demonstrates that the decoupling of Re and Os is enhanced in coarse-grained molybdenite. Further, single molybdenite grain and grain fragments yield erroneous age data that deviate by 5-25% from the reproducible dates determined from the pulverised sample. Thus, such sample material should never be used to obtain age data. The Re-Os data show that the 'critical' factor in obtaining an accurate Re-Os molybdenite date is a homogeneous representation of the Re and Os in the sample in the analyzed aliquot. Analytical protocols that include sampling, sample preparation and aliquot size are 'key' to obtaining accurate and reproducible Re-Os dates for molybdenite. The results of this study preclude the application of in-situ ( $\mu\text{m}$ ) analysis such as laser-ablation-ICPMS on molybdenite to obtain an accurate Re-Os date.

### References

- Stein, H.J., Markey, R. J., Morgan, J. W., Hannah, J. L. And Scherstén, A., (2001), *Terra Nova*, **13**, 479-486.