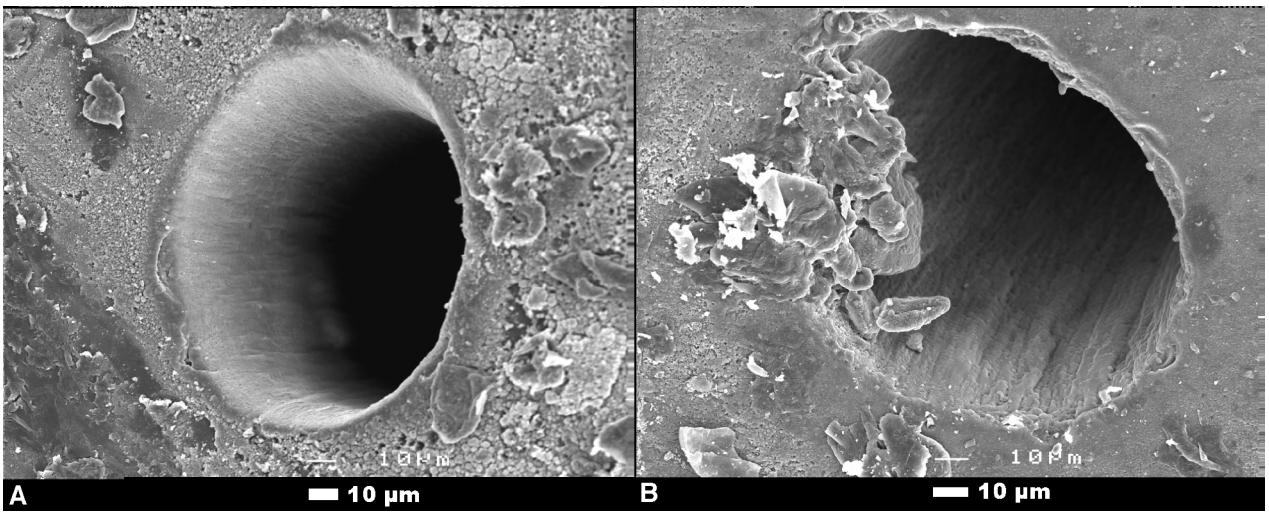

Figure 1. A. SEM image of ablation crater in xerogel. B. Showing spalling. Surface non-orthogonal to image

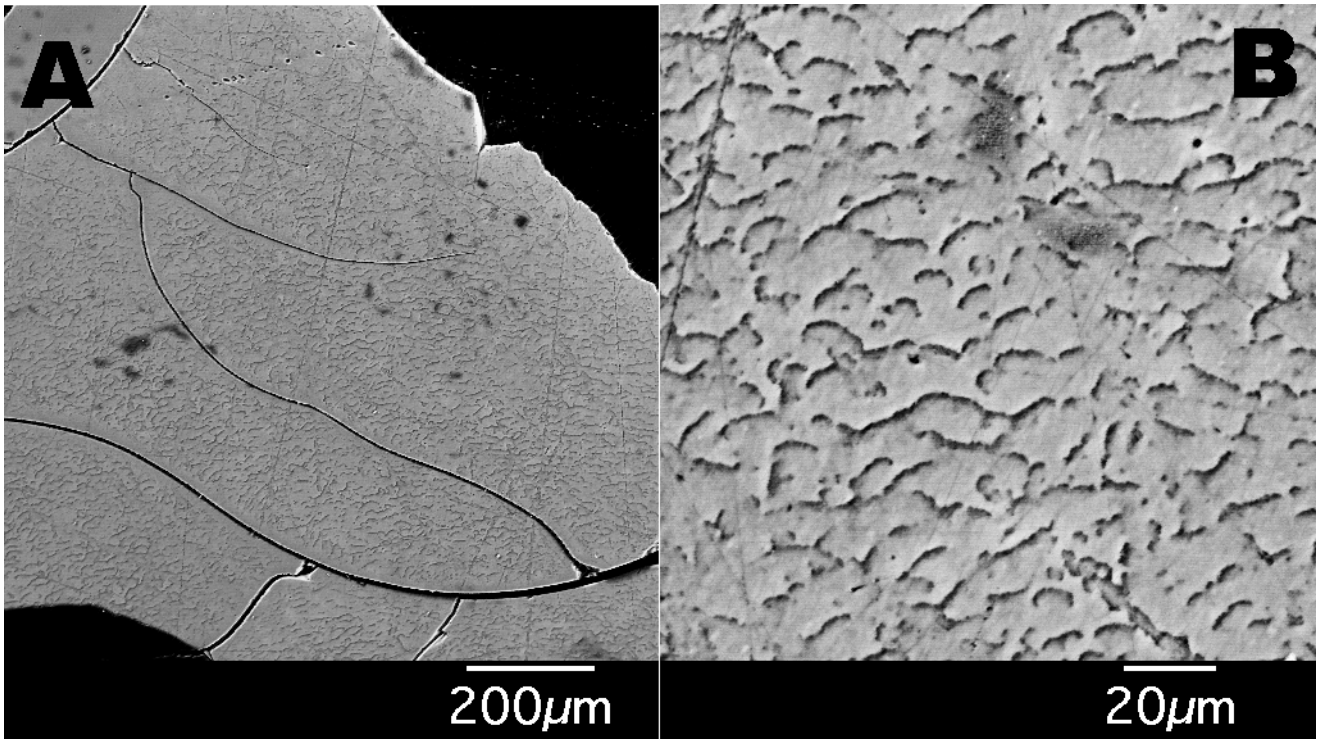

Figure 2. Electron backscatter images of xerogels. Darker patches in upper centre of B are thinner portions of the thin section (also observed under optical microscopy). Linear features are of topographic origin

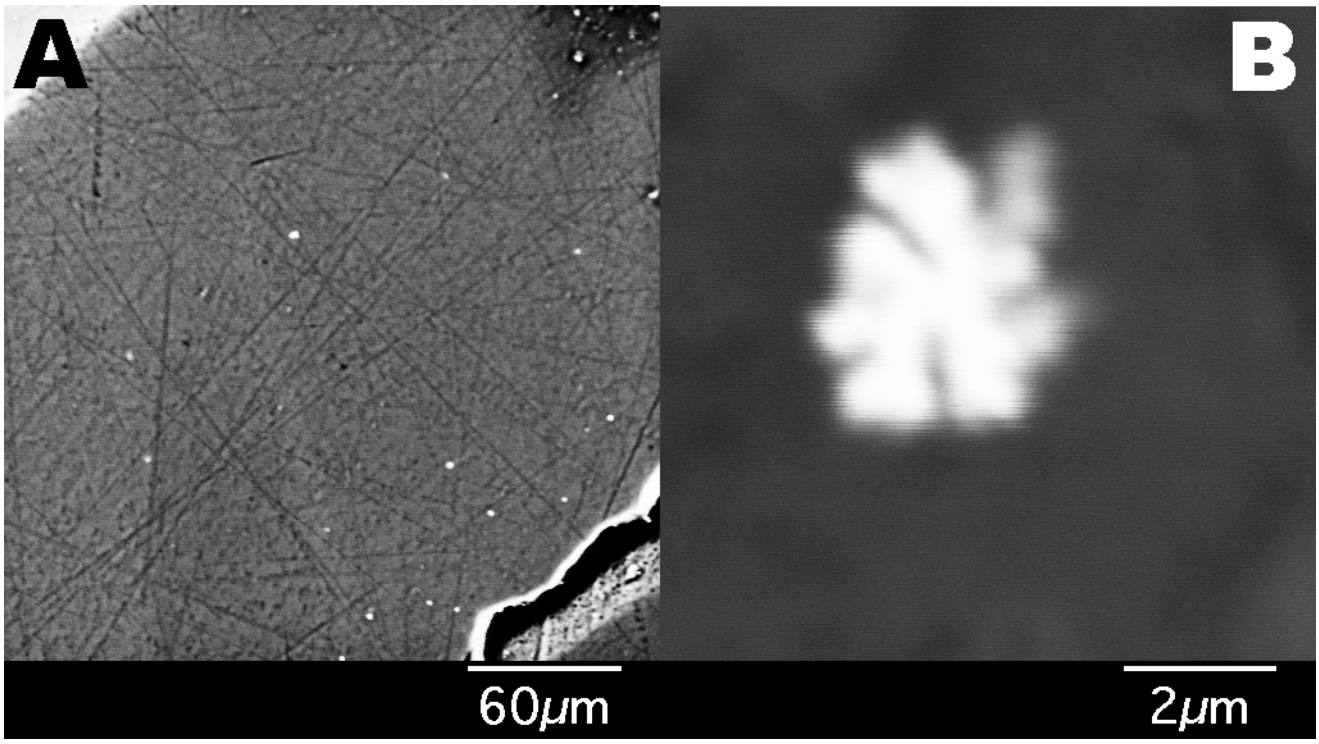

Figure 3. Electron backscatter image of series 5 xerogel (SG5A) with selenium, sulphur and metal rich inclusions [bright spots] (A), with close-up of inclusions (B)

Additional Analytical Techniques

Bulk Selenium Analysis (NAA)

Selenium in xerogels is determined by neutron activation analysis (NAA) at the Centre for Neutron Activation at McMaster University. Samples are ground in the same fashion as for sulphur analysis. A sample aliquot is transferred into a pre-cleaned high-density polyethylene vial and heat-sealed. Standards and blanks are similarly prepared. For the determination of selenium, samples are irradiated for 7 seconds in a thermal irradiation site (nominal flux $5x10^{+12}$ n cm^{-2} s^{-1}), with a delay to count of 7 seconds and a counting time of 30 seconds. Gamma spectra to quantitate ^{76}Se and ^{77m}Se are collected with a hyper-pure germanium detector (efficiency 20%, FWHM 1.8 keV at 1332 keV) on a PC based multi channel analyzer. The photopeak at 161.9 keV is integrated to quantitate the selenium. The system is calibrated with in-house selenium standards and certified reference materials are analyzed as unknowns with each run.

Bulk Sulphur Analysis

Sulphur concentration and isotope ratios are measured with a MAT-252 IRMS (Thermo Finnigan) coupled to a NCS 2500 elemental analyzer (Thermo Electron) optimized for sulphur isotope ratio determinations. Xerogels are hand-ground to sand size with a pestle in an agate mortar. Weighed aliquots of samples are placed in tin cups and sealed. Physical limitations of sample size result in a detection limit of 200 μg g^{-1} sulphur. The concentration analysis is calibrated by a DL-methionine standard and isotope abundances are calibrated by certified and in-house isotope reference standards[1]. Duplicate analyses indicate an uncertainty in concentration of 10% and 0.3 per mil in the sulphur isotopic compositions.

Scanning electron microscopy and electron microprobe analysis

Electron microscope examination of xerogels is made using the JEOL 6400 digital scanning electron microscope at Carleton University (Ottawa, Ontario). Xerogels are placed on aluminum slides and sputter coated by gold and palladium. Full details of theory and practice are available elsewhere[2, 3].

Electron microprobe analysis is by a Camebax MBX electron microprobe also at Carleton University. EMPA samples are polished thin sections of xerogel fragments coated by a carbon film. A 15kV beam is used with a 40 second measurement counting time and a 80 second background counting time. Calibration is based on in-house mineral standards. Detection limits are ~100 μg g^{-1} for both selenium and sulphur[4]. Full details of the operations and theory are available elsewhere[2, 3].

1. A. Rainbow, A. H. Clark, T. K. Kyser, F. Gaboury and C. J. Hodgson, *Chem. Geol.*, 2005, **215**, 235-252.
2. J. Goldstein, D. E. Newbury, P. Echlin, D. C. Joy, A. D. J. Romig, C. E. Lyman, C. Fiori and E. Lifshin, *Scanning Electron Microscopy and X-Ray Microanalysis: A Text for Biologists, Materials Scientists, and Geologists*, Plenum, New York. 1992.
3. P. J. Potts, J. F. W. Bowles, S. J. B. Reed and M. R. Cave, eds., *Microprobe Techniques in the Earth Sciences*, New York, Chapman & Hall. 1995.
4. P. Jones, 2005, Personal Communication

Table 1. Concentrations of sulphur and selenium in natural and reference sulphide materials

	Type	S	Se	Se/S
CCu-1c[a]	Cu concentrate (pressed disc)	33.3±0.3 wt. %	107±15 μg g^{-1}	3.21±0.45 x 10^{-4}
PS-1	Synthetic sulphide (pressed disc)	27.6 wt.%	53 μg g^{-1}	1.92±0.19 x 10^{-4}
Horne14CPY	Chalcopyrite	34.9±0.7 wt. %	384±58 μg g^{-1}	9.97±1.52 x 10^{-4}
Horne16CPY	Chalcopyrite	34.9±0.7 wt. %	418±63 μg g^{-1}	11.98±1.82 x 10^{-4}
Horne18CPY	Chalcopyrite	34.9±0.7 wt. %	383±60 μg g^{-1}	10.97±1.73 x 10^{-4}
Horne19CPY	Chalcopyrite	34.9±0.7 wt. %	300±41 μg g^{-1}	8.60±1.19 x 10^{-4}
Horne16PY	Pyrite	53.5±2.7 wt. %	498±75 μg g^{-1}	9.38±1.49 x 10^{-4}
Horne20PY	Pyrite	53.5±2.7 wt. %	754±113 μg g^{-1}	14.09±2.23 x 10^{-4}
Horne21PY	Pyrite	53.5±2.7 wt. %	300±45 μg g^{-1}	5.61±0.88 x 10^{-4}
T25	Synthetic selenide	2.3±0.2 wt. %	22.8±0.2 wt. %	9.91±0.99
T26	Synthetic selenide	4.8±0.5 wt. %	17.7±0.5 wt. %	3.69±0.38
T27	Synthetic sulphide	7.5±0.8 wt. %	12.2±0.8 wt. %	1.62±0.19
T28	Synthetic sulphide	10.3±0.6 wt. %	6.4±0.6 wt. %	0.62±0.07

[a] Certified values

Table 2. Available sulphur and selenium concentrations for NIST SRM glasses

Element	Analytical Method	Sample Size	Concentration μg g^{-1}	Reference
NIST SRM 610				
Sulphur	Laser plasma ionization mass spectrometry	Fragment	456±32	[1]
	Secondary ionization mass spectrometry	Multiple Spots	693±194	[2]
Selenium	Particle induced x-ray emissions	Multiple Spots	108.0±4.5	[3]
	Particle induced x-ray emissions	Multiple Spots	110±6	[4]
	Particle induced x-ray emissions	Multiple Spots	114±7	[4]
	Particle induced x-ray emissions	Multiple Spots	183±16	[1]
NIST SRM 612				
Sulphur	Laser ablation spark source mass spectrometry	Spot	16±2 (n=1)	[5]
	Secondary ionization mass spectrometry	Multiple Spots	350±35	[2]
Selenium	ICPMS	1 mg	59±1	[6]
	ICPMS	10 mg	20.0±4.3 (n=81)	[7]
	ICPMS	200 mg	19.0±2.2 (n=10)	[8]

Table 3. Analyte contents, Se/S concentration ratios and $\delta^{34}S$ values of xerogels (Atmosph. Isol. = Atmospheric Isolation, Gravi. = Gravimetric, Anal. = Analysis)

		S μg g^{-1}			Se μg g^{-1}					Pb	Fe
Xerogel	Atmosph. Isol.	Gravi.	Anal.	Loss %	Gravi.	Anal.	Loss %	Se/S	$\delta^{34}S_{CDT}$ ‰	μg g^{-1} Gravi.	
SG3I	Moderate	682±68	506±25	25	591±59	587±59	~0	1.16±0.13 x 10^{0}	14.1	Not present	
SG3J	Moderate	613±61	591±30	3	723±72	732±73	~0	1.24±0.14 x 10^{0}	14.1		
SG3L	High	359±36	311±15	13	550±50	470±47	~0	1.51±0.16	12.5		

SG10A	Low	842±84	209±10	75	8±1	7±1	~0	x 10^{0} 3.34±0.36	13.6		
SG5A[a]	Low	593±60	-	-	75±8	85±9	~0	x 10^{-2} -	14.3	131±13	188±19

[a] Not used for calibration

Table 4. Typical relative standard deviations of the $^{77}Se/^{32}S$ signal ratio from multiple ablation spots and combined concentration uncertainty

Standard/Xerogel Series	Signal Ratio RSD %	Combined S & Se concentration uncertainty %
NIST SRM 610	20	Unknown
NIST SRM 612	25	Unknown
CCu-1c	15	14
PS-1	15	10
HORNE16CPY	10	15
HORNE19CPY	15	14
SG10	10	25
SG3	10	11

Table 5. Electron microprobe analysis of xerogels and NIST SRM 610; with analysis of inclusion and matrix in SG5A and comparison to bulk composition (Rel. var. = relative variation)

	Number of measurements	Si	Se		S		Pb	Fe
		Wt. %	$\mu g\ g^{-1}$	Rel. var.	$\mu g\ g^{-1}$	Rel. var.	$\mu g\ g^{-1}$	$\mu g\ g^{-1}$
NIST SRM 610	5	31.78±0.18	214±121	57%	508±35	7%	Not measured	
SG3J	8	37.60±0.40	159±56	35%	370±65	18%	Not Present	
SG3L	12	33.11±1.02	723±114	16%	839±263	31%	Not Present	
SG10A	3	34.52±0.10	165±75	45%	430±67	16%	Not Present	
SG5A								
Inclusions	1	32.54±0.22	2400±700	29%	3600±500	14%	26900±800	790±121
Matrix	7	34.11±0.17	100±100	100%	500±100	20%	100±100	300±100
Bulk[a]	N/A	33[b]	70±10	14%	590±10	2%	131±10[c]	188±10[c]

[a] Other methods

[b] Theoretical, based on SiO_2 composition and 30 wt. % residual fluid

[c] Gravimetric calculation

1. A. B. E. Rocholl, K. Simon, K. P. Jochum, F. Bruhn, R. Gehann, U. Kramar, W. Luecke, M. Molzahn, E. Pernicka, M. Seufert, B. Spettel and J. Stummeier, *Geostand. Newsl.*, 1997, **21**, 101-114.

2. K. P. Jochum, B. Stoll, K. Herwig, M. Willbold, A. W. Hofmann, M. Amini, S. Aarburg, W. Abouchami, I. Raczek, A. Stracke, O. Alard, C. Bouman, S. Becker, M. Dücking, H. Brätz, R. Klemd, D. de Bruin, D. Canil, D. Cornell, J. C. M. De Hoog, C. Dalpé, L. V. Danyushevsky, A. Eisenhauer, Y. Gao, J. E. Snow, N. Groschopf, D. Günther, C. Latkoczy, M. Guillong, E. Hauri, H. E. Höfer, L. Y., K. Horz, D. E. Jacob, S. Kasemann, A. J. R. Kent, T. Ludwig, T. M. Zack, P. R. D., A. Meixner, M. Rosner, K. Misawa, B. P. Nash, J. A. Pfänder, W. R. Premo, D. Sun Weidong, M. Tiepolo, R.

Vannucci, T. Vennemann, D. Wayne and J. D. Woodhead, *Geochem. Geophys. Geosyst.*, 2006, **7**, doi:10.1029/2005GC001060.
3. T. M. Benjamin, C. J. Duffy and P. S. Z. Rodgers, *Nucl. Instum. Methods Phys. Res., Sect. B.*, 1988, **B30**, 454-458.
4. P. S. Z. Rogers, C. J. Duffy and T. M. Benjamin, *Nucl. Instum. Methods Phys. Res., Sect. B.*, 1987, **B22**, 133-137.
5. R. W. Bonham and J. C. Quattlebaum, *Spectroscopy International*, 1989, **1**, 42-44.
6. A. Zurhaar and L. Mullings, *J. Anal. At. Spectrom.*, 1990, **5**, 611-617.
7. D. C. Duckworth, C. K. Bayne, S. J. Morton and J. Almirall, *J. Anal. At. Spectrom.*, 2000, **15**, 821-929.
8. T. Parouchais, I. M. Warner, L. T. Palmer and H. Kobus, *J. Forensic Sci.*, 1996, **41**, 351-360.